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RUTHENATE ION CATALYSED OXIDATION OF SOME UNSATURATED ALCOHOLS BY ALKALINE HEXACYANOFERRATE(III) ION[1]

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Abstract—The kinetics of ruthenate ion catalysed oxidation of allyl alcohol, crotyl alcohol, cinnamyl alcohol and propargyl alcohol by hexacyanoferrate(III) ion in an aqueous alkaline media at constant ionic strength indicate no dependence of rate on alkali concentration or ionic strength. The reaction shows first order dependence on ruthenate ion and zero order in hexacyanoferrate(III) ion. The rate of the reaction increases with increase in substrate concentration and shows Michaelis–Menten type of behaviour. The data suggests that the oxidation proceeds via the formation of a complex between an alcohol molecule and ruthenate ion yielding corresponding acids. The reaction has been studied at four different temperatures and thermodynamic parameters have been computed. A plausible mechanism consistent with the experimental results is proposed.

Transition metal ions Ru(III), Os(VIII) and Ru(VIII) with co-oxidants, oxidise several organic compounds in acidic as well as in alkaline media.[2-5] Such studies prompted us to study the kinetics of Ru(VI) catalysed oxidation of some primary and secondary alcohols[6] by hexacyanoferrate(III) ion in aqueous alkaline medium. On extension of our previous work we are reporting kinetics of Ru(VI) catalysed oxidation of allyl, crotyl, cinnamyl and Propargyl alcohols by alkaline hexacyanoferrate(III). The ionic strength of the reaction mixture has been kept constant by addition of sodium perchlorate because perchlorate ion does not form complex with ruthenate ion.[7]

EXPERIMENTAL

The substrates allyl alcohol (May & Baker A. R.), crotyl alcohol (E. Merck G. R.), cinnamyl alcohol (Bush-repacked G. R.) and propargyl alcohol (Riedel A. G.) were redistilled before use. Ruthenium dioxide (Johnson Matthey & Co, England) was used for the preparation of sodium ruthenate and all other chemicals used were BDH AnalaR grade.

The sodium ruthenate solution was prepared by the oxidation of hydrated ruthenium dioxide with metaperiodate and reducing thus produced ruthenium tetraoxide by the action of carbonate free sodium hydroxide.[8] The purity of the solution of ruthenate ion was checked by finding out the ratio of absorbance at 460 and 385 nm as 2.07 corresponding to pure ruthenate.[9] The concentration of ruthenate ion was determined by measuring the absorbance at 460 nm, 1820 $cm^{-1}M^{-1}$ being its molar absorbity coefficient, with the help of Beckman DU-2 model spectrophotometer.

The progress of the reaction was followed by measuring disappearance of hexacyanoferrate(III) with Spekol spectrophotocolorimeter at 420 nm. In most of the cases the reaction was followed upto 50–70% completion. The values obtained from repeated runs were agree within 2–3%.

RESULTS AND DISCUSSION

The stoichiometric studies show that one molecule of alcohol consumes four molecules of hexacyanoferrate(III). The reactions can be represented as follows:

$$RCH_2OH + 4Fe(CN)_6^{3-} + 5CH^- \xrightarrow{Ru(VI)} RCO\bar{O} + 4Fe(CN)_6^{4-} + 4H_2O$$

where R stands for CH_2=CH, HC=C, CH_3CH=CH, and C_6H_5CH=CH.

Products were isolated by solvent extraction method. Each product has separately been identified by paper chromatography. In all cases solvent was taken as butanol saturated with ammonia. Paper strip was then allowed to dry, the paper was sprayed with bromophenol blue solution in acetone and warmed for a short time to accelerate the reaction with product. A yellow spot[10] confirms the presence of corresponding carboxylic acids.

The kinetics of oxidation of allyl alcohol, crotyl alcohol, cinnamyl alcohol and propargyl alcohol by alkaline hexacyanoferrate(III) using sodium ruthenate as a homogeneous catalyst at constant ionic strength has been followed at several initial concentrations of reactant. The standard zero order rate constant (k_s) presented in the table averages two runs at least.

Figure 1 shows a typical zero order plot for each alcohol. It is obvious from these plots that the reaction velocity remains constant even upto 60–70% of the reaction. Table 1 clearly indicates that zero order rate constants (k_s) are fairly constant but the value of k_s is slightly higher at higher concentration of hexacyanoferrate(III) ion which may be due to the small contribution towards rate by the step (III) in the proposed mechanism. It is quite evident from Fig. 2 that the rate is directly proportional to ruthenate ion concentration, and these graphs have unit slope which indicates that order is unity with respect to ruthenate ion. The effect of variation of alcohol concentration on the velocity of the reaction exhibits the Michaelis–Menten[11] plots (Fig. 3), i.e. an intercept is obtained on k_s^{-1} axis showing thereby the complex formation between ruthenate ion and an alcohol molecule.

Before proposing the oxidation scheme, it is worthwhile to discuss the probable species of Ru(VI). Electronic spectra studies have confirmed that lower oxidation state of ruthenium exists in hydrated form but the higher oxidation state are not strongly solvated.[12] There is no evidence for addition of $O\bar{H}$ ion to 3d metal oxo anions[8] but in case of reaction between perruthenate and manganate ion[13] in alkaline medium it was suggested that one or more of the anions could possibly have hydroxide

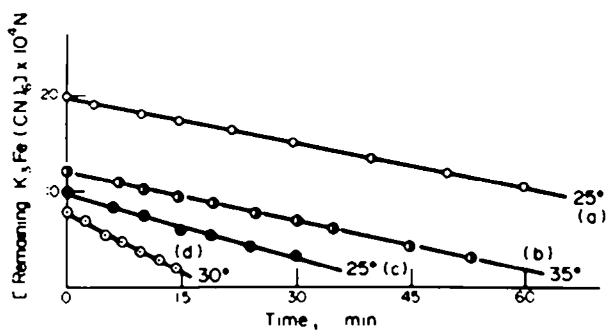

Fig. 1. [OH] = 5.0×10^{-2} M, $\mu = 0.26$ M: (A) [crotyl alcohol] = 6.7×10^{-3} M, [Ru(VI)] = 15.1×10^{-7} M: (B) [propargyl alcohol] = 2.0×10^{-2} M, [Ru(VI)] = 10.0×10^{-7} M; (C) [cinnamic alcohol] = 5.0×10^{-3} M, [Ru(VI)] = 15.8×10^{-7} M; (D) [allyl alcohol] = 2.5×10^{-2} M, [Ru(VI)] = 5.6×10^{-7} M.

Table 1. Effect of hexacyanoferrate(III) on the rate of oxidation

(A)								
[NaOH] = 5.0×10^{-2} M, [Crotyl alcohol] = 6.7×10^{-3} M, [Ru(VI)] = 1.5×10^{-7} M								
Temp. = 25°, $\mu = 0.26$ M								
$[Fe(CN)_6^{-3}] \times 10^4$ M =	25.0	20.0	12.5	10.0	8.25	6.25	5.0	4.0
$k_s \times 10^6$ M · min^{-1} =	20.3	19.8	19.2	19.2	19.0	18.8	18.7	18.5
(B)								
Temp. = 35°, $\mu = 0.26$ M								
[NaOH] = 5.0×10^{-2} M [Propargyl alcohol] = 2.0×10^{-2} M [Ru(VI)] = 10.0×10^{-7} M								
$[Fe(CN)_6^{-3}] \times 10^4$ M =	25.0	20.0	12.5	10.0	8.30	6.66	5.0	4.0
$k_s \times 10^6$ M · min^{-1} =	38.2	37.6	37.1	37.0	36.8	36.5	36.5	36.3
(C)								
Temp. = 25°, $\mu = 0.26$ M								
[NaOH] = 5.0×10^{-2} M, [Cinnamic alcohol] = 5.0×10^{-3} M, [Ru(VI)] = 15.8×10^{-7} M								
$[Fe(CN)_6^{-3}] \times 10^{-4}$ M =	20.0	12.5	10.0	8.25	7.14	6.25	5.0	4.0
$k_2 \times 10^6$ M, min^{-1} =	20.2	19.8	19.6	19.4	19.4	19.1	18.9	18.8
(D)								
Temp. = 35°, $\mu = 0.26$ M								
[NaOH] = 5.0×10^{-2} M, [Allyl alcohol] = 2.5×10^{-2} M, [Ru(VI)] = 5.6×10^{-7} M								
$[Fe(CN)_6^{-3}] \times 10^{-4}$ M =	20.0	12.50	10.0	8.25	7.14	6.25	5.0	4.0
$k_s \times 10^6$ M · min^{-1} =	51.1	50.0	49.7	59.6	49.1	49.0	48.6	48.2

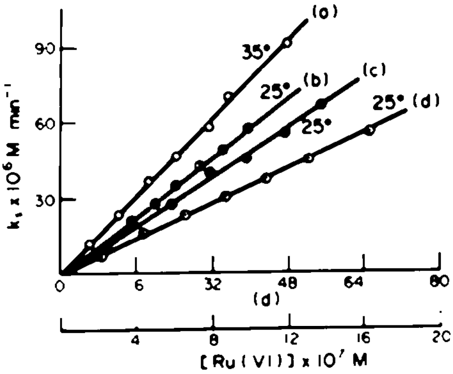

Fig. 2. $[K_3Fe(CN)_6] = 12.5 \times 10^{-4}$ M, [OH] = 5.0×10^{-2} M, $\mu = 0.26$ M: (A) [propargyl alcohol = 1.0×10^{-2} M; (B) [crotyl alcohol] = 1.1×10^{-2} M; (C) [cinnamic alcohol] = 5.0×10^{-3} M; (D) [allyl alcohol] = 1.0×10^{-2} M.

ion associated with them and coordination of $\bar{OH}$ ion with per ruthenate upto lower extent has also been suggested by Syman and coworkers[14] during the kinetic study of decomposition of perruthenate ion in alkaline medium therefore during the kinetic study it can be assumed that ruthenium(VI) remains as ruthenate ion, i.e. RuO_4^{-2}.

$$RuO_4^{-2} + S \overset{K_1}{\rightleftharpoons} (\text{complex})^{-2} \qquad (1)$$

$$(\text{Complex})^{-2} \xrightarrow[\text{Slow}\ x\ H_2O]{k} RuO_2 \cdot xH_2O + \bar{OH} + \text{Aldehyde} \qquad (ii)$$

$$RuO_2 \cdot x \cdot H_2O + 2Fe(CN)_6^{-3} + 4OH \xrightarrow{\text{fast}}$$

$$RuO_4^{-2} + 2Fe(CN)_6^{-4} + (x+2)H_2O \qquad (iii)$$

$$RCHO \xrightarrow[\text{Ru(VI)}\ Fe(CN)_6^{-3} \cdot \bar{OH}]{\text{fast}} RCO\bar{O} \qquad (iv)$$

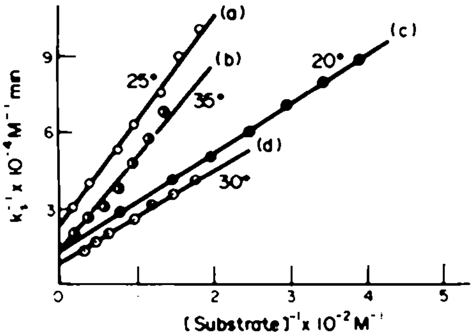

Fig. 3. $[K_3Fe(CN)_6] = 12.5 \times 10^{-4}$ M, $[OH^-] = 5.0 \times 10^{-2}$ M, μ = 0.26 M: (A) [Ru(VI)] = 4.4×10^{-7} M; (B) [Ru(VI)] = 10.0×10^{-7} M, (C) [Ru(VI)] = 2.4×10^{-7} M; (D) [Ru(VI)] = 15.1×10^{-7} M.

where S stands for allyl alcohol, crotyl alcohol, cinnamyl alcohol and propargyl alcohol and R stands for CH_2=CH, CH_3CH_2=CH, C_6H_5·CH=CH and HC≡C-groups.

The first step of proposed mechanism involves the formation of complex between ruthenate ion and substrate. The complex thus formed undergoes slow disproportionation giving reduced form of ruthenium as ruthenium dioxide, i.e. Ru(IV), and corresponding aldehyde. Ruthenium dioxide produced in step (II) is immediately oxidised to ruthenate ion by hexacyanoferrate(III) and alkali. The separate experiments have been carried out without addition of hexacyanoferrate(III), a black precipitate was produced which is nothing but ruthenium dioxide. This black precipitate was washed several times with water and mixed with little amount of alkaline hexacyanoferrate(III). Resulted solution was capable of catalysing the oxidation of studied compounds. Thus step (II) is justified in proposed mechanism. The test tube experiments show that the oxidation of aldehyde is very fast under experimental conditions, therefore aldehyde produced in step (II) immediately oxidised to corresponding acid in step (IV). The product study also shows the production of acid. Hence step (VI) proposed in above scheme is justified.

The rate of oxidation in terms of decreasing concentration of hexacyanoferrate(III) can be written as

$$-\frac{d[Fe(CN)_6{}^{3}]}{dt} = k[(Complex)]^{-2}. \qquad (1)$$

From the step (i) the concentration of complex is given as

$$[(Complex)^{2}] = K_1[S][RuO_4{}^{-2}] \qquad (2)$$

The total concentration of ruthenate ion would be given as

$$[RuO_4{}^{2}]_T = [(Complex)]^{2} + [RuO_4{}^{2}] \qquad (3)$$

where T stands for total

On substituting the value of complex from eqn (2) in eqn (3).

$$[RuO_4{}^{-2}]_T = K_1[S][RuO_4{}^{2}] + [RuO_4{}^{-2}] \qquad (4)$$

$$[RuO_4{}^{2}] = \frac{[RuO_4{}^{-2}]_T}{1 + K_1[S]}. \qquad (5)$$

Now the rate expression in terms of total concentration of ruthenate ion, considering the equation (1), (2) and (5) can be written as

$$-\frac{[d(Fe(CN)_6{}^{3-}]}{dt} = \frac{kK_1[S][RuO_4{}^{2}]_T}{1 + K_1[S]}. \qquad (6)$$

The rate law is consistent with the observed results should be given in terms of actual decrease in the concentration of hexacyanoferrate(III) and eqn (6) would be written as

$$-\frac{d[Fe(CN)_6{}^{3-}]}{dt} = \frac{4kK_1[S][RuO_4{}^{2}]_T}{1 + K_1[S]}. \qquad (7)$$

The factor "four" in eqn (7) is introduced because stoichiometric studies shows that four molecules of hexacyanoferrate(III) are consumed by one molecule of alcohol.

The rate expression (7) clearly explains the observed experimental results, i.e. velocity is directly proportional to ruthenate ion concentration, (Fig. 2) and also Michaelis–Menten[11] behaviour with respect to substrate (Fig. 3). The rate expression (7) can be rearranged as

$$\frac{1}{Rate} = \frac{1}{4kK_1[S][RuO_4{}^{-2}]_T} + \frac{1}{4k[RuO_4{}^{2}]_T} \qquad (8)$$

where

$$-\frac{d[Fe(CN)_6{}^{3}]}{dt} = Rate = k_s.$$

The value of K_1 (the formation constant of the complex) and *k* (the disproportionation constant of the complex) has been calculated with the help of graph $(rate)^{-1}$ vs $[Substrate]^{-1}$ (Fig. 3). The values of K_1 and k are given in Table 2. The value of K_1 has also been calculated with the help of the slope of the graph · k_s vs [Ru(VI)] (Fig. 2). It is quite evident from Table 2 that the value K_1 obtained from both plots are quite close to each other which further supports the proposed mechanism.

Having obtained the value of k and K_1 for all four

Table 2.

Alcohol	K_1 from $(Rate)^{-1}$ vs $substrate^{-1}$ plot	K_1 from (Rate) vs [Ru(VI)] plot	k min^{-1}	ΔE_a kj/mole	ΔS^* J/degree	ΔG^* kj/mole
Allyl (25°)	60.0	58.1	23.8	61.0	− 120.3	97.4
Crotyl (25°)	40.0	45.5	10.0	57.2	− 129.7	96.5
Propargyl (35°)	30.6	30.0	21.8	57.4	− 136.1	98.4
Cinnamyl (20°)	77.0	80.0	7.0	52.6	− 138.9	94.7

Table 3. $[K_3Fe(CN)_6] = 12.5 \times 10^{-4}$ M; $[OH^-] = 5.0 \times 10^{-2}$ M, $\mu = 0.26$ *M*

	$[Ru(VI)] \times 10^7$ M	$k_e \times 10^6$ M·min^{-1} (calculated)	$k_e \times 10^6$ M·min^{-1} (observed)
[Allyl Alcohol] × 10^2 M (25°)			
5.0	4.4	31.2	31.9
1.25	4.4	18.4	18.7
0.83	4.4	13.8	13.4
1.0	2.2	7.7	7.7
1.0	6.56	22.9	22.9
[Crotyl Alcohol] × 10^2 M (25°)			
1.1	5.02	7.2	7.71
1.1	20.1	28.5	28.1
3.3	15.1	35.5	36.1
2.0	15.1	30.4	31.0
1.0	15.1	18.9	19.4
[Cinnamyl Alcohol] × 10^2 M (20°)			
1.00	23.7	27.1	27.9
0.25	23.7	10.1	10.7
0.5	7.9	6.3	6.2
0.5	31.6	25.2	24.9
0.5	55.3	44.2	43.2
[Propargyl Alcohol] × 10^2 M (35°)			
5.0	10.0	53.0	51.1
2.5	10.0	37.6	36.8
1.0	10.0	20.3	21.0
1.0	3.1	6.2	6.1
1.0	12.5	25.0	24.5

alcohols and substituting these values in rate expression (7) for each alcohol, the eqn (7) can be written as (for allyl alcohol).

$$\frac{-[\mathrm{Fe(CN)_6}^{3-}]}{dt} = \frac{4 \times 23.8 \times 60[\mathrm{RuO_4}^{-2}]_T[\text{allyl alcohol}]}{1 + 60[\text{allyl alcohol}]}. \tag{9}$$

Similar expressions can also be written for rest of the three alcohols. The validity of rate law (7) is further verified by comparing the observed and calculated values of the reaction rates from eqn (9). Five runs under different experimental conditions have been examined and corresponding values of the reaction rate from eqn (9) have also been calculated for each alcohol and results are given in Table 3.

It is now evident from Table 3 that the value of k_e observed and k_e calculated are in close agreement (± 1.5%) which again supports the validity of eqn (7) and hence the proposed mechanism.

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