

Kinetics of ruthenium(III)-catalysed oxidation of aromatic aldehydes by alkaline ferricyanide

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Abstract. The ruthenium(III)-catalysed ferricyanide oxidation of aromatic aldehydes in aqueous alkaline medium follows a zero order kinetics with respect to ferricyanide. The order with respect to Ru(III) is unity. The variation of substrate concentration follows Michaelis-Menton type of kinetics. The dependence on alkali is fractional below 0.05 M and tends to be independent above 0.05 M. The reaction proceeds through the reversible complexation between Ru(III) and the hydrated aldehyde, which decomposes in a rate determining step, giving the products. The structure reactivity relationship has been analysed in the light of Hammett's plot.

Keywords. Oxidation; kinetics; aromatic aldehydes; ferricyanide; Ru(III) catalysed oxidation.

1. Introduction

Although potassium ferricyanide an one-electron oxidant with a redox potential of +0.36 eV has been used for the oxidation of many substrates, the oxidation of aromatic aldehydes with alkaline ferricyanide is not facile. In the earlier communication (Radhakrishnamurti and Sahu 1978) the oxidation of benzaldehyde and substituted benzaldehydes by alkaline ferricyanide catalysed by OsO₄ has been reported. The present study deals with the oxidation of aromatic aldehydes by alkaline hexacyanoferrate(III)-catalysed by Ru(III).

2. Materials and methods

The aldehydes were of AR grade and were either redistilled or recrystallised before use. Potassium ferricyanide and Ruthenium(III) chloride were also of AR grade. The solution of ruthenium trichloride was prepared according to the procedure adopted by Singh *et al* (1977). Kinetic runs were followed by estimating the residual ferricyanide by standard iodometric method.

3. Stoichiometry

The overall stoichiometry is aldehyde : ferricyanide (1 : 2) for all the compounds studied and the products are the corresponding benzoic acids, which have been identified by the usual spot tests.

4. Results and discussion

The reactions are zero order in the oxidant, although individual runs show a curvature at higher percentages of the reaction. Such deviations in individual runs were noticed earlier by Littler (1962) in the oxidation of cyclohexanone and by Radhakrishnamurti and Sahu (1978) in the OsO_4 catalysed oxidation of benzaldehydes. Further, the reaction is complicated at higher percentages due to the formation of ferrocyanide. The plots of $[\text{Fe}(\text{CN})_6]^{3-}$ vs time are linear thereby showing the typical zero order rates for the oxidation of benzaldehydes in the presence of Ru(III), the rate constants are computed from the initial percentages of the reactions. The data in table 1 show that the values of $k_0(-dc/dt)$ are fairly constant for different ferricyanide concentrations. This confirms the zero order dependence of the reaction rate with respect to ferricyanide.

The rate constants for the various substrates studied are reported in table 2. The results presented indicate that the $k_0/[S]$ values decrease with increase in the concentration of the substrate following Michaelis-Menton type kinetics, k_0 being the rate constant computed with respect to the oxidant. Such a trend towards lower order at higher concentrations of substrate has been observed by

Table 1. Effect of varying [ferricyanide] on the rate of catalysed oxidation of aromatic aldehydes by ferricyanide.

[Substrate] = 1.0×10^{-3} M, [Ru(III) chloride] = 1.9×10^{-6} M		[NaOH] = 0.1 M Temp. = 50° C	
10^3 [ferricyanide] M		$10^6 k_0$ M. min ⁻¹	
	Benzaldehyde		
0.6259		2.018	
0.8935		2.065	
1.187		2.31	
1.481		2.115	
1.778		1.932	
	<i>m</i> -nitro benzaldehyde		
0.6186		21.83	
0.9152		23.87	
1.217		24.34	
1.552		24.51	
1.813		24.73	

Table 2. Effect of varying [substrate] on the rate of catalysed oxidation of aromatic aldehydes by ferricyanide.

[Ferricyanide] = 1.2×10^{-3} M [Ru(III) chloride] = 1.9×10^{-6} M			[NaOH] = 0.1 M, Temp. = 50° C		
10^3 [substrate] M	$10^6 k_0$ M. min ⁻¹	$10^3 k_1 (= k_0/S)$ min ⁻¹			
Benzaldehyde					
1.104	2.558	2.317			
2.264	4.565	2.017			
5.00	9.047	1.809			
10.00	17.19	1.719			
15.00	25.97	1.732			
20.00	33.06	1.653			
25.18	41.11	1.632			
<i>o</i> -nitro benzaldehyde					
1.006	25.64	25.49			
2.088	40.78	19.53			
<i>m</i> -nitro benzaldehyde					
1.005	24.34	24.22			
2.00	39.29	19.64			
3.00	45.07	15.02			
<i>p</i> -nitro benzaldehyde					
1.00	25.74	25.74			
2.128	40.78	19.17			

Radhakrishnamurti and Sahu (1978) in the oxidation of aliphatic alcohols and diols by alkaline ferricyanide catalysed by Ru(III).

Increase in the concentration of ruthenium(III) chloride, increases the rate (table 3) and plots of $\log k_0$ versus $\log [\text{Ru(III)}]$ are linear with unit slopes confirming the first order dependence on ruthenium(III) chloride.

Above 0.05M alkali concentration for all the compounds under study the reaction rate is independent of [alkali]. Below this concentration the alkali dependence is fractional ranging from 0.35 to 0.8 depending upon the nature of the substituents (table 4). This may be attributed to the equilibrium between the hydrated form and the free aldehyde molecule. Above 0.05 M alkali it is only the hydrated species that participates in the reaction.

The effect of addition of potassium chloride on the oxidation rate is found to be negligible and the addition of potassium ferrocyanide has a retarding effect on the rate, indicating that there is no influence of ionic strength on the reaction rate and pointing thereby the ion-dipole nature of the reaction.

Table 3. Effect of varying [Ru(III) chloride] on the rate of oxidation of aromatic aldehydes by ferricyanide.

[Ferricyanide] = 1.2×10^{-3} M, [NaOH] = 0.1 M, Temp. = 50° C		
[Substrate] = 0.001 M	10^5 [Ru(III)] M	$10^6 k_0$ M. min ⁻¹
Benzaldehyde	1.90	2.317
	3.80	4.256
	5.70	6.667
	7.60	9.09
	9.50	11.09
<i>o</i> -nitro benzaldehyde	0.95	12.90
	1.90	25.49
	2.85	38.50
	3.80	48.45
<i>m</i> -nitro benzaldehyde	0.95	12.11
	1.90	24.22
	2.85	36.84
	3.80	48.84
<i>p</i> -nitro benzaldehyde	0.95	12.87
	1.90	25.74
	2.85	37.12
	3.80	50.07
<i>p</i> -chloro benzaldehyde	0.95	2.845
	1.90	5.552
	2.85	8.153
	3.80	10.64
<i>p</i> -tolualdehyde	1.9	1.259
	3.8	2.446
	5.7	4.295
	7.6	5.808

The effect of change of structure on the reaction kinetics has been investigated and the rate constants for various substrates studied, reported in table 2, indicate the order of reactivity is *p*-nitro- \sim *o*-nitro- \sim *m*-nitro- $>$ *p*-chloro- $>$ benzaldehyde $>$ *p*-tolualdehyde. This shows that electron withdrawing groups accelerate the oxidation process while electron releasing groups retard it. Plot of $\log k_0$ versus σ is linear with a ρ value of +1.41 suggesting two electron transfer (figure 1). Such two electron transfer has already been invoked earlier by Wiberg and Stewart (1955) in the oxidation of benzaldehyde by permanganate in alkaline medium with a ρ value of +1.83.

The effect of temperature on the reaction rate are collected in table 5.

Electronic spectra studies by Connick and Fine (1960) have confirmed that ruthenium(III) chloride exists in the hydrated form as $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$. In alkaline medium (Cotton and Wilkinson, 2nd Edition, 1972) $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ also exists in the

Table 4. Effect of varying [NaOH] on the rate of catalysed oxidation of aromatic aldehydes by ferricyanide.

[Ferricyanide] = 1.2×10^{-3} M, [Ru(III) chloride] = 1.9×10^{-6} M,		
		Temp. = 50° C
[Substrate] = 0.001 M	[NaOH] M	$10^6 k_p$ M min ⁻¹
Benzaldehyde	0.009	1.75
	0.024	1.964
	0.050	2.093
	0.10	2.317
	0.152	2.277
	0.204	2.270
	0.250	2.376
	0.304	2.376
<i>o</i> -nitro benzaldehyde	0.009	6.18
	0.024	11.02
	0.05	21.86
	0.10	25.49
	0.15	29.29
	0.20	29.19
	0.25	29.65
	0.30	29.41
<i>m</i> -nitro benzaldehyde	0.1	7.607
	0.025	14.04
	0.05	22.64
	0.10	24.22
	0.15	23.13
	0.20	24.22
	0.25	23.48
<i>p</i> -nitro benzaldehyde	0.01	7.987
	0.024	14.85
	0.05	24.42
	0.10	25.74
	0.15	26.77
	0.202	26.17
	0.25	25.88
	0.304	24.98
<i>p</i> -chloro benzaldehyde	0.0045	3.558
	0.0095	4.007
	0.025	4.343
	0.05	5.321
	0.10	5.552
	0.15	6.119
	0.20	6.142
	0.25	6.29
<i>p</i> -tolualdehyde	0.005	1.174
	0.0095	2.384
	0.024	2.506
	0.05	2.518
	0.10	2.446
	0.15	2.412
	0.20	2.747

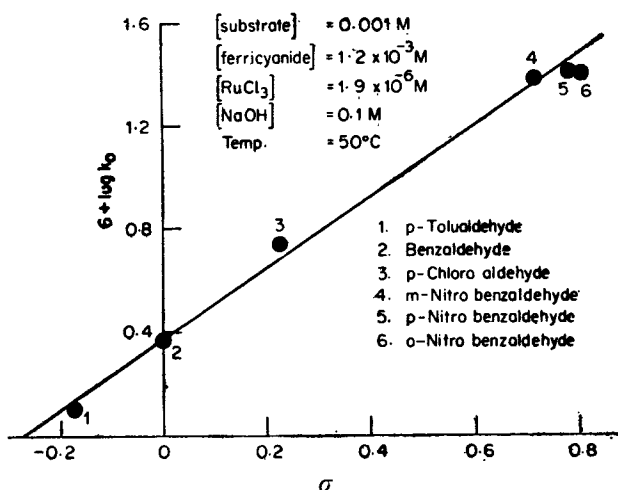


Figure 1.

Table 5. Effect of temperature on the reaction rates.

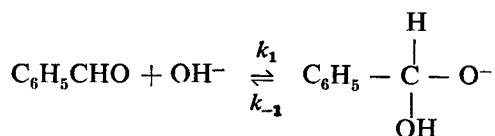
[Ferricyanide] = 1.2×10^{-3} M,
 [Ru(III)] = 1.9×10^{-6} M

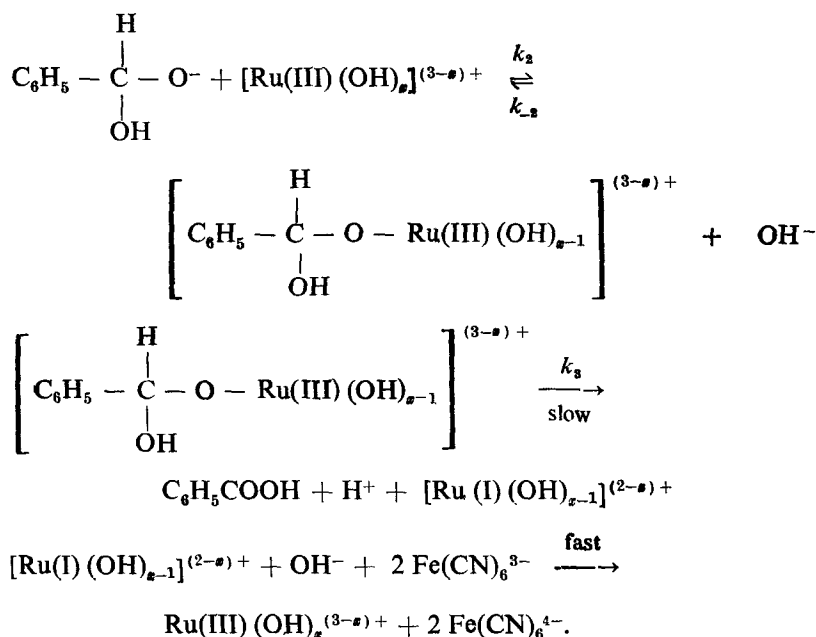
[NaOH] = 0.1 M

[Substrate] = 0.001 M	$10^8 k_0$ M. sec ⁻¹		
	40° C	50° C	60° C
Benzaldehyde	3.07	3.86	5.72
<i>o</i> -nitro benzaldehyde	28.53	42.48	60.33
<i>m</i> -nitro benzaldehyde	28.28	40.37	60.33
<i>p</i> -nitro benzaldehyde	28.27	42.90	61.75
<i>p</i> -chloro benzaldehyde	6.49	9.253	12.48
<i>p</i> -tolualdehyde	1.603	2.097	2.99

form $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$. It is quite probable that in the present study the species form $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ might assume the general form $[\text{Ru}(\text{H}_2\text{O})_{6-x}(\text{OH})_x]^{(3-x)+}$, where the value of x will be less than six as there is no definite evidence of any hexahydroxy species of ruthenium (Griffith 1967).

From the above observations the possible mechanism for the Ru(III)-catalysed oxidation of aldehydes is given as :





The hydrated aldehyde complexes with Ru(III) and the complex breaks down in a rate determining step to give the products. Ru(I) generated is reconverted by ferricyanide to Ru(III) in a fast step. The products in all the cases have been identified to be the corresponding benzoic acids.

The above postulated mechanism leads to the following rate law:

$$[\text{Ru}]_T = [\text{Ru}] + \text{complex} \quad (\text{C})$$

$$\left[\text{C}_6\text{H}_5 \begin{array}{c} \text{O}^- \\ | \\ \text{CHOH} \end{array} \right] (x) = \frac{k_1 [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-]}{k_{-1}}$$

$$k_2 [x] [\text{Ru}] = k_{-2} [\text{complex}] [\text{OH}^-] + k_3 [\text{complex}]$$

$$[\text{complex}] = \frac{k_2 [x] [\text{Ru}]^{+3}}{k_3 + k_{-2} [\text{OH}^-]}$$

$$\begin{aligned}
 [\text{Ru}]_T^{+3} &= [\text{Ru}]^{+3} + \frac{k_2 [x] [\text{Ru}]^{+3}}{k_3 + k_{-2} [\text{OH}^-]} \\
 &= [\text{Ru}]^{+3} + \frac{k_2 [\text{Ru}]^{+3} \frac{k_1}{k_{-1}} [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-]}{k_{-2} [\text{OH}^-] + k_3} \\
 &= [\text{Ru}]^{+3} \left\{ 1 + \frac{\frac{k_1 k_2}{k_{-1}} [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-]}{k_3 + k_{-2} [\text{OH}^-]} \right\}
 \end{aligned}$$

$$\begin{aligned}
 &= [\text{Ru}] \left\{ \frac{k_3 + k_{-2} [\text{OH}^-] + \frac{k_1 k_2}{k_{-1}} [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-]}{k_3 + k_{-2} [\text{OH}^-]} \right\} \\
 [\text{Ru}]^{+3} &= \frac{[\text{Ru}]_T \{k_{-3} + k_{-2} [\text{OH}^-]\}}{k_3 + k_{-2} [\text{OH}^-] + \frac{k_1 k_2}{k_{-1}} [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-]} \\
 \text{Rate} &= k_3 [\text{complex}] \\
 &= \frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = 2k_3 [\text{complex}] \\
 &= \frac{2k_3 k_2 \frac{k_1}{k_{-1}} [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-] [\text{Ru}]^{+3}}{k_3 + k_{-2} [\text{OH}^-]} \\
 &= \frac{2k_3 k_2 k_1 [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-] [\text{Ru}]_T \{k_3 + k_{-2} [\text{OH}^-]\}}{k_{-1} \{k_3 + k_{-2} [\text{OH}^-]\} \left\{ k_3 + k_{-2} [\text{OH}^-] + \frac{k_1 k_2}{k_{-1}} [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-] \right\}} \\
 &= \frac{2k_1 k_2 k_3 [\text{C}_6\text{H}_5\text{CHO}] [\text{OH}^-] [\text{Ru}]_T^{+3}}{k_{-1} \left[k_3 + [\text{OH}^-] \left\{ k_{-2} + \frac{k_1 k_2}{k_{-1}} [\text{C}_6\text{H}_5\text{CHO}] \right\} \right]}
 \end{aligned}$$

The above rate law explains all the orders observed with respect to Ru(III) alkali and substrate.

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