

CHAPTER V

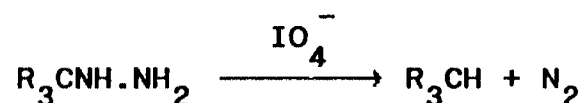
RUTHENIUM(III) CATALYZED OXIDATION OF ALLYL ALCOHOL BY PERIODATE IN AQUEOUS ALKALINE MEDIUM.

The activity of periodate as an oxidizing agent varies greatly as a function of pH and is capable of subtle control. In acid solution, it is one of the most powerful oxidizing agents known, quantitatively and rapidly converting manganese(II) salts to permanganate, while in alkaline solution, it is slightly less oxidizing than hypochlorite. In alkaline medium, periodate is known to exist as different species involving multiple equilibria¹ and it needs to know the active form of oxidant in the reaction.

Despite the ease with which periodate perform all the oxidations, effected by iodate, periodates have not been used in inorganic preparative and analytical operations; titration with NaIO_4 has been suggested as a method of analyzing² mixtures of S^{2-} , SO_3^{2-} , HSO_3^- , $\text{S}_2\text{O}_4^{2-}$ and $\text{S}_2\text{O}_3^{2-}$.

However, there are numerous reports of the oxidation of organic compounds by periodic acid or periodates³ not merely

in conjunction with perchloric acid in the "wet fire" destructive oxidation of organic compounds⁴, but as reagents able to execute a number of well defined reactions. The specific cleavage of 1,2-diols has widely been exploited in the realm of carbohydrates and nucleic acids, and the mechanism has been well established. In rigid systems only *cis* - functional groups are oxidized, the specificity being due to the cyclic intermediate. Periodate has also been applied to the oxidation of phenols (to quinones), sulfides (to sulphoxides) and hydrazine derivatives:

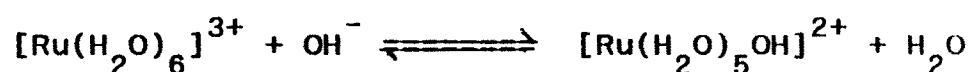


The importance of allyl alcohol in a number of industries is mentioned in the Chapter IV (p. 147). The oxidation of allyl alcohol by various oxidants studied has also been reported in Chapter IV (p. 147).

Pioneering and incisive studies on the catalytic activity of transition metal ions in the oxidation of organic molecules have paved way to newer fields in kinetics. In recent years osmium, iridium and ruthenium compounds have been found to be efficient homogeneous catalysts in numerous redox processes.

The genesis of the catalytic activity of transition metal ions emerges from the presence of vacant d-orbitals which readily accommodate electrons temporarily and coupled with this is the normal redox potential of the oxidized and reduced form of the catalyst. The use of transition metal ions such as ruthenium, osmium, iridium etc. either alone or binary mixtures as catalysts⁵ in the oxidation of several redox processes is of considerable interest. Though the mechanism of catalysis depends on the nature of substrate, oxidant, and other experimental conditions, it has been⁶ shown that metal ions act as catalyst by one of these different paths like formation of a complex with reactants or free radicals etc.

The use of RuCl_3 as a homogeneous catalyst in both acidic and alkaline media is of recent interest. Ruthenium(III) catalysis in redox reactions involve several complexities due to the formation of different intermediate complexes and variable oxidation states of ruthenium. In alkaline media, the following equilibrium exists.



In catalysis, ruthenium(III) suffers either a one electron

transfer or two electron transfer. Transient ruthenium(I) or ruthenium(II) species are reconverted to ruthenium(III) by the oxidant. In some cases involving outer-sphere hydride abstraction, the valence state of ruthenium(III) remains unchanged.

Even though periodate is very potent oxidant in acid medium, the oxidation of allyl alcohol by periodate did not take place even in presence of active catalysts like ruthenium, osmium etc.. Hence we have investigated the kinetics of oxidation of allyl alcohol by periodate catalysed by Ru(III) in aqueous alkaline medium. Herein we report the results of such study.

EXPERIMENTAL

All the chemicals used were of reagent grade and doubly distilled water was used throughout the work. The stock solutions of periodate were prepared by dissolving a known weight of potassium meta periodate (Riedel) in water and were used after keeping for 24 h. The concentration of the solution was verified by titration with standard sodium thiosulphate iodometrically⁷ at neutral pH maintained by potassium phosphate, dibasic (K_2HPO_4) and potassium phosphate,

monobasic (KH_2PO_4) using starch as an indicator.

The preparation of stock solution of allyl alcohol and sodium thiosulphate and their standardization is explained in Chapter IV (p. 151).

The stock solution of ruthenium(III) solution was made by dissolving RuCl_3 (S.D.fine) in 0.20 mol dm^{-3} HCl . Mercury is added to reduce any Ru(IV) formed during the preparation and kept for a day. Its concentration was ascertained by EDTA titration⁸.

Sodium perchlorate which was found to be inactive was used to maintain constant ionic strength and sodium hydroxide (AnalaR) was used to get the required alkalinity. Potassium iodate (KIO_3) solution was prepared by dissolving a known amount of potassium iodate (Reechem) in water.

Kinetic Procedure

All kinetic runs were carried out under pseudo-first order conditions at $25.0 \pm 0.1^\circ\text{C}$ unless otherwise stated. The reaction was initiated by mixing previously thermostatted solutions of periodate and allyl alcohol, which also contained

the required amounts of NaOH and NaClO₄ as a source of alkali and ionic strength in different stoppered bottles. The first solution contained the required concentrations of substrate, allyl alcohol, sodium hydroxide and sodium perchlorate and the second solution was that of oxidant, periodate, of required concentration. The reaction was followed by determining the concentration of unreacted periodate as follows : 5.0 cm³ of reaction mixture was pipetted into an iodine flask containing 5.0 cm³ of 10% potassium iodide solution and a calculated amount of potassium phosphate (dibasic) was added just to neutralize the alkali and to bring the pH of the resulting solution to 5.0-5.5. The iodine liberated by periodate was titrated against standard sodium thiosulphate solution using starch as an indicator. Under these conditions, IO₃⁻ was without any effect on the added I⁻ and IO₄⁻ was quantitatively reduced to IO₃⁻. Such titrations were carried out at regular intervals of time.

At room temperature and in alkaline medium allyl alcohol was not hydrolysed to any significant extent. No effect of dissolved oxygen on the rate of reaction was found.

As the IO₄⁻ oxidation of allyl alcohol in alkaline medium

proceeds with measurable rate in the absence of Ru(III), the catalyzed reaction is understood to occur in parallel paths with contributions from both the catalyzed and uncatalysed paths. Thus the total rate constant (k_T) is equal to the sum of rate constants of the catalyzed (k_C) and uncatalysed (k_U) reactions. Thus $k_C = k_T - k_U$. Hence in this case order of reaction was found from logarithmic plots of k_C versus concentrations. It was found that at different initial concentrations of periodate, the plots of $\log [IO_4^-]$ versus time were linear up to more than two half lives of the reaction. This showed an unit order dependence on the periodate concentration which is also supported by the constancy of rate constants at different concentrations of periodate. The duplicate runs were reproducible within $\pm 5\%$. An example run is shown in Table V(i) (p. 193).

Table V(1)

Ru(III) catalyzed oxidation of allyl alcohol by periodate in
aqueous alkaline medium at 25°C

Example run

$$[\text{IO}_4^-] = 4.0 \times 10^{-3};$$

$$[\text{AA}] = 4.0 \times 10^{-2};$$

$$[\text{OH}^-] = 0.20;$$

$$\text{Ru(III)} = 5.0 \times 10^{-6};$$

$$I = 0.60/\text{mol dm}^{-3};$$

Time min	Burette Reading (0.005 M $\text{Na}_2\text{S}_2\text{O}_3$) cm^3	$[\text{IO}_4^-]$ $\times 10^3$ mol dm^{-3}
0.0	7.8	3.90
2.0	7.4	3.70
4.0	7.2	3.60
6.0	7.1	3.55
10.0	6.9	3.45
20.0	6.0	3.00
35.0	5.2	2.60
50.0	4.6	2.30
60.0	3.8	1.90
70.0	3.1	1.55
80.0	2.6	1.30
100.0	2.0	1.00
120.0	1.8	0.90
140.0	1.4	0.70
160.0	1.1	0.55
180.0	0.8	0.40

Error \pm 5%

RESULTS

Stoichiometry

Different sets of reaction mixtures containing different concentrations of periodate and allyl alcohol at constant concentrations of sodium hydroxide and sodium perchlorate and Ruthenium(III) were allowed to react for 24 h at 25°C and then analyzed. When periodate concentration was higher than that of allyl alcohol, the total oxidant concentration was found by iodometry⁷ and after accounting for the remaining oxidant concentration, the concentration of iodate formed was derived. While, under the condition, $[AA] > [IO_4^-]$, when the periodate had fully reacted, the unreacted allyl alcohol was estimated as in Chapter IV (p. 151). Acrolein was found to be the main product as evidenced by spot test as explained in chapter IV (p. 155). Test for acrylic acid was negative (Chapter IV (p. 155) Another product, iodate was determined iodometrically in 1.0 mol dm⁻³ sulphuric acid. The results were in agreement with a 1:1 stoichiometry (equation 1) (Table V(ii) (p. 195).

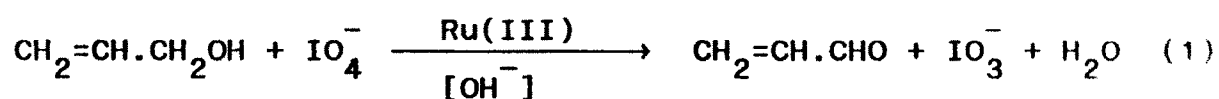


Table V(ii)

Stoichiometry of oxidation of allyl alcohol by periodate in aqueous alkaline medium at 25.0 °C

$[\text{OH}^-] = 0.20 ;$

$I = 0.60/\text{mol dm}^{-3};$

$[\text{IO}_4^-]^*$ $\times 10^2$ taken	$[\text{AA}]^*$ $\times 10^2$ taken	$[\text{IO}_4^-]^*$ $\times 10^2$ found	$[\text{AA}]^*$ $\times 10^2$ found	$[\text{IO}_3^-]^*$ $\times 10^2$ found
1.0	3.0	--	2.0	1.00
1.0	1.0	--	--	1.03
0.5	1.0	--	0.5	0.50
1.0	0.5	0.56	--	0.47

Error \pm 5%

* All concentrations are in mol dm^{-3}

REACTION ORDER

The kinetic runs of Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium were followed at different initial concentrations of oxidant, substrate, alkali and Ru(III) in turn keeping all other concentrations constant. With increase of each of $[\text{IO}_4^-]$, $[\text{AA}]$, $[\text{OH}^-]$ and $[\text{Ru(III)}]$ showed the positive dependence on the rate of the reaction. The orders were obtained from the $\log k_c$ versus \log (concentration) plots and k_c were reproducible to within $\pm 5\%$.

Effect of Varying [Periodate]

The periodate concentration was varied in the range of 1.0×10^{-3} to 1.0×10^{-2} mol dm⁻³ at constant concentration of allyl alcohol, alkali, Ru(III) and sodium perchlorate as in Table V(iii) (p. 197). From the plots of $\log[\text{IO}_4^-]$ versus time, the order in periodate concentration was observed as unity as shown in Fig.V(i) (p. 198).

Effect of Varying [Allyl Alcohol]

From the plot of $\log k_c$ versus $\log [\text{AA}]$, the order in $[\text{AA}]$ was found to be less than unity in the concentration range 2.0×10^{-2} to 2.0×10^{-1} mol dm⁻³ as shown in Table V(iii) (p. 197) and Fig.V(i) (p. 198).

Table V(III)

Effects of variation of $[\text{IO}_4^-]$ and $[\text{AA}]$ on Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium at 25°C

$$[\text{OH}^-] = 0.20;$$

$$[\text{Ru(III)}] = 5.0 \times 10^{-6};$$

$$I = 0.60/\text{mol dm}^{-3};$$

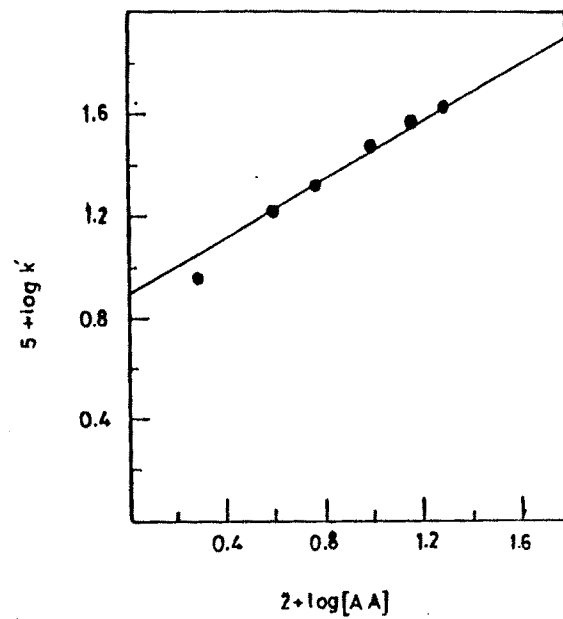
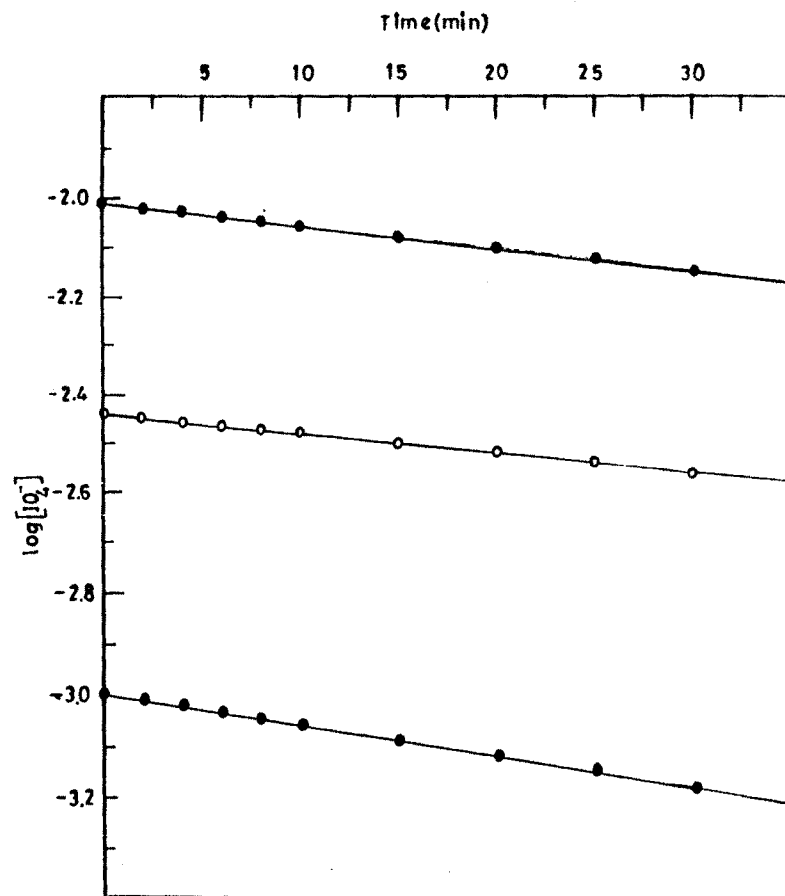
$[\text{IO}_4^-]$ $\times 10^3$ mol dm^{-3}	$[\text{AA}]$ $\times 10^2$ mol dm^{-3}	k_T $\times 10^5$ s^{-1}	k_u $\times 10^5$ s^{-1}	k_c $\times 10^5$ s^{-1}	* Exptl.	* Calcd.
1.0	4.0	22.12	6.52	15.60	15.63	
2.0	4.0	22.13	6.52	15.61	15.63	
3.0	4.0	22.15	6.52	15.63	15.63	
4.0	4.0	22.14	6.52	15.62	15.63	
6.0	4.0	22.12	6.52	15.60	15.63	
10.0	4.0	22.15	6.52	15.63	15.63	
4.0	2.0	12.29	3.37	8.92	8.92	
4.0	4.0	22.15	6.52	15.63	15.63	
4.0	6.0	30.32	9.47	20.85	20.87	
4.0	10.0	43.31	14.85	28.46	28.49	
4.0	15.0	55.55	20.74	34.81	34.87	
4.0	20.0	65.06	25.87	39.19	39.27	

Error \pm 5%

* Experimental and Calculated

Figure V(1)

Order in $[\text{IO}_4^-]$ and $[\text{AA}]$: on Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline
(Conditions as in the Table V(iii) p. 197)



Effect of Varying [Alkali]

The alkali concentration was varied in the range of 5.0×10^{-2} to 5.0×10^{-1} mol dm⁻³ keeping all other conditions being constant as given in Table V(iv) (p. 200). From the plot of log k_c versus log [OH⁻] as shown in Fig.V(ii) (p. 201) the order with respect to alkali was less than unity.

Effect of Varying [Catalyst]

The order with respect to [Ru(III)] was one as evident from the plot of log k_c versus log [Ru(III)] as shown in the Fig.V(ii) (p. 201) when its concentration was varied from 1.0×10^{-6} to 1.0×10^{-5} mol dm⁻³ at constant [oxidant], [alkali] [substrate] and ionic strength as in Table V(iv) (p. 200).

Effect of Added Products

The effect of initially added product, iodate and acrolein, each in the concentration range of 1.0×10^{-3} to 8.0×10^{-3} mol dm⁻³ keeping all other conditions being constant was studied and did not affect rate of reaction as shown in the Table V(v) (p. 202).

Table V(iv)

Effects of variation of $[\text{OH}^-]$ and $[\text{Ru(III)}]$ on Ru(III)
catalyzed oxidation of allyl alcohol by periodate
in aqueous alkaline medium at 25°C

$$[\text{IO}_4^-] = 4.0 \times 10^{-3};$$

$$[\text{AA}] = 4.0 \times 10^{-2}$$

$$I = 0.60/\text{mol dm}^{-3}$$

$[\text{OH}^-]$ x 10 mol dm^{-3}	$[\text{Ru(III)}]$ x 10 ⁶ mol dm^{-3}	k_T x 10 ⁵ s^{-1}	k_U x 10 ⁵ s^{-1}	k_C x 10 ⁵ s^{-1}	* Exptl.	* Calcd.
0.5	5.0	7.91	2.42	5.49		5.48
1.0	5.0	13.84	4.16	9.68		9.67
1.5	5.0	18.47	5.50	12.97		12.97
2.0	5.0	22.15	6.52	15.63		15.63
3.0	5.0	24.66	8.00	19.66		19.68
5.0	5.0	34.68	9.90	24.78		24.82
2.0	1.0	9.65	6.52	3.13		3.13
2.0	3.0	16.40	6.52	9.38		9.38
2.0	5.0	22.15	6.52	15.63		15.63
2.0	7.0	28.40	6.52	21.88		21.89
2.0	9.0	34.65	6.52	28.13		28.14
2.0	10.0	37.78	6.52	31.26		31.27

Error \pm 5%

* Experimental and Calculated

Figure V(11)

Order in $[\text{OH}^-]$ and $[\text{Ru(III)}]$: on Ru(III) Catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium
(Conditions as in Table V(iv) p. 200)

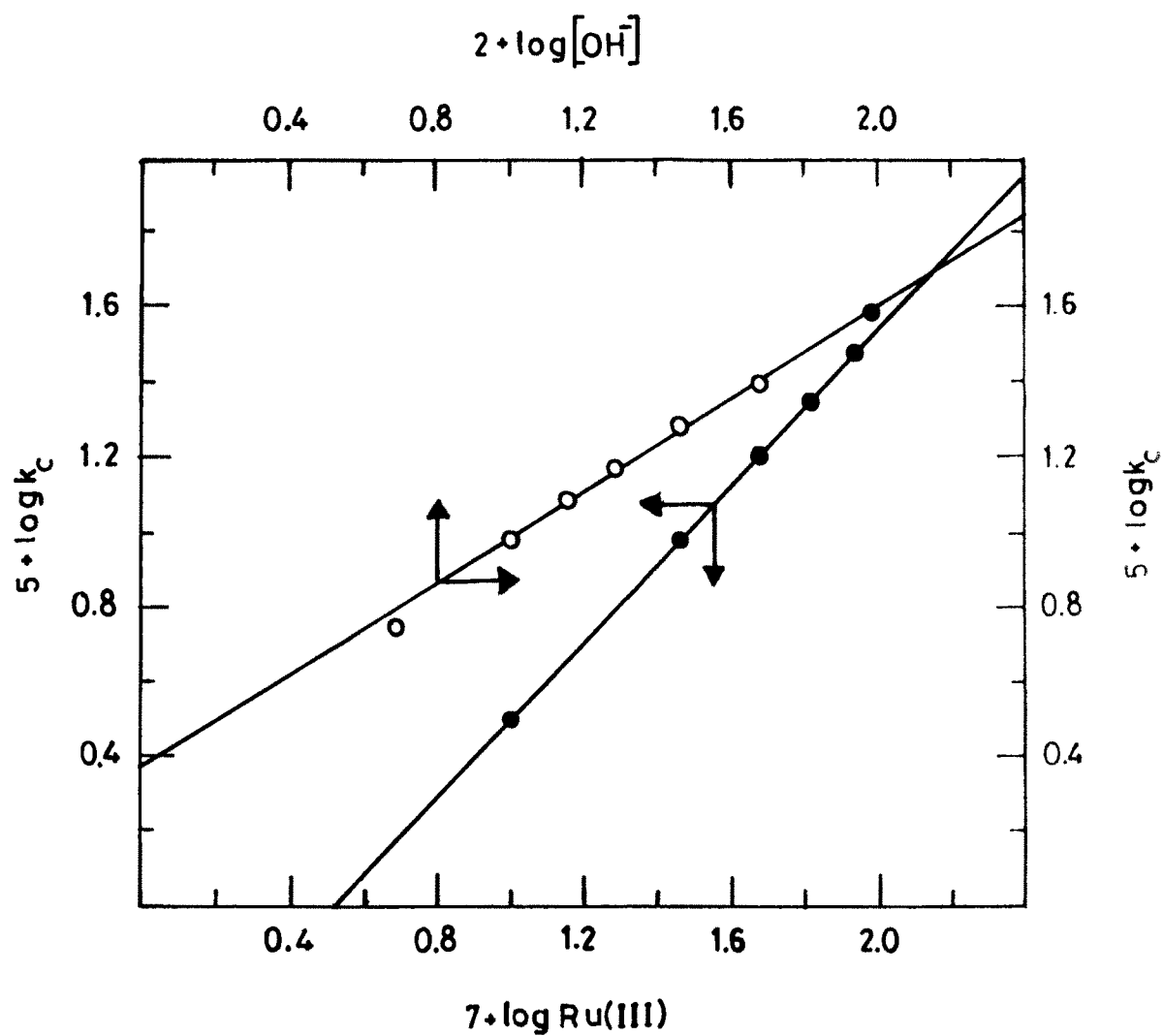


Table V(v)

Effect of initially addition of product on Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium at 25°C

$$[\text{IO}_4^-] = 4.0 \times 10^{-3};$$

$$[\text{OH}^-] = 0.20;$$

$$[\text{AA}] = 4.0 \times 10^{-2};$$

$$\text{Ru(III)} = 5.0 \times 10^{-6};$$

$$I = 0.60/\text{mol dm}^{-3};$$

$[\text{IO}_3^-]$ $\times 10^3$ mol dm^{-3}	[Acrolein] $\times 10^3$ mol dm^{-3}	k_c $\times 10^5$ s^{-1}
1.0	-	15.68
2.0	-	15.60
4.0	-	15.73
6.0	-	15.64
8.0	-	15.76
-	1.0	15.64
-	2.0	15.67
-	4.0	15.73
-	6.0	15.60
-	8.0	15.68

Effect of Dielectric Constant

The dielectric constant (D) of the reaction medium was varied by using t-butanol-water content (v/v) in the reaction mixture with all other conditions being constant as given in the Table V(vi) (p. 204). The dielectric constants of the reaction medium at different compositions of t-butanol and water mixtures were calculated as given in chapter I (p. 57). It is found that with increase of t-butanol content in the reaction mixture from 0.0 to 40.0 % (v/v) the rate remained almost unchanged has shown in the Table V(vi) (p. 204).

Effect of Ionic Strength

The ionic strength of reaction medium was varied from 6.0×10^{-2} to $6.0 \times 10^{-1} \text{ mol dm}^{-3}$ using sodium perchlorate at constant concentrations of oxidant, reductant, alkali and catalyst as in Table V(vi) (p. 204). No appreciable change in the reaction rate was observed as shown in the Table V(vi) (p. 204) indicating the negligible effect of ionic strength on the reaction rate.

Table V(vi)

Effect of dielectric constant (D) and ionic strength (I) on
Ru(III) catalyzed oxidation of allyl alcohol by periodate
in aqueous alkaline medium at 25° C

$$[\text{IO}_4^-] = 4.0 \times 10^{-3};$$

$$[\text{AA}] = 4.0 \times 10^{-2};$$

$$[\text{OH}^-] = 0.20;$$

$$\text{Ru(III)} = 5.0 \times 10^{-6};$$

$$I = 0.60/\text{mol dm}^{-3}$$

* % of (v/v)	D	k_c $\times 10^5$ s^{-1}	I mol dm^{-3}	k_c $\times 10^5$ s^{-1}
0.0	78.5	15.68	0.06	15.83
5.0	75.1	15.79	0.12	15.66
10.0	71.7	15.73	0.20	15.68
20.0	65.0	15.76	0.40	15.62
30.0	58.2	15.64	0.50	15.71
40.0	51.5	15.71	0.60	15.83

* % of t-butanol

Test for Free Radicals

The intervention of the free radicals in the reaction was examined as follows: the reaction mixture, to which a known quantity of acrylonitrile had been added initially, was kept for 24 h in an inert atmosphere. On diluting the reaction mixture with methanol a copious precipitate resulted suggesting the possibility of free radical intervention in the reaction scheme.

Effect of Temperature

The rate constants (k) of the slow step of the scheme 1 were obtained from the slopes and intercepts of $1/k_c$ versus $1/[AA]$ and $1/k_c$ versus $1/[OH^-]$ plots at four different temperatures. The values of k ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) were found to be 3.3×10^2 , 4.8×10^2 , 6.5×10^2 and 8.7×10^2 at 298, 303, 308 and 313 K respectively. These data were subjected to least square analysis and are tabulated in the Table V(vii) (p. 206). From the slope of the plot of $\log k$ versus $1/T$ as shown in the Fig.V(iii) (p. 207) the activation parameters have been calculated as in Chapter I and are given in Table V(viii) (p. 208). The activation parameters for uncatalysed reaction are also given in Table V(viii) (p. 208).

Table V(vii)

Effect of temperature on Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium

$$[\text{IO}_4^-] = 4.0 \times 10^{-3};$$

$$[\text{AA}] = 4.0 \times 10^{-2};$$

$$[\text{OH}^-] = 0.20;$$

$$I = 0.60;$$

$$\text{Ru(III)} = 5.0 \times 10^{-6} / \text{mol dm}^{-3};$$

Temp	k	1/T (x)	logk (y)	XY	X ²	Y _{cal.}
	$\times 10^{-2}$	$\times 10^3$				
K	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	K^{-1}		$\times 10^3$	$\times 10^5$	
298	3.29	3.35	2.517	8.431	1.122	2.49
303	4.79	3.30	2.680	8.844	1.089	2.61
$\Sigma x = 6.65 \times 10^{-3}$		$\Sigma xy = 17.27 \times 10^{-3}$		$\Sigma x^2 = 2.202 \times 10^{-5}$		
313	6.46	3.24	2.810	9.104	1.049	2.75
318	8.71	3.19	2.940	9.378	1.076	2.87
$\Sigma x = 6.43 \times 10^{-3}$		$\Sigma x = 18.48 \times 10^{-3}$		$\Sigma x^2 = 2.056 \times 10^{-5}$		

Figure V(iii)

Effect of temperature on Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium
(Conditions as in Table V(vii) p. 206)

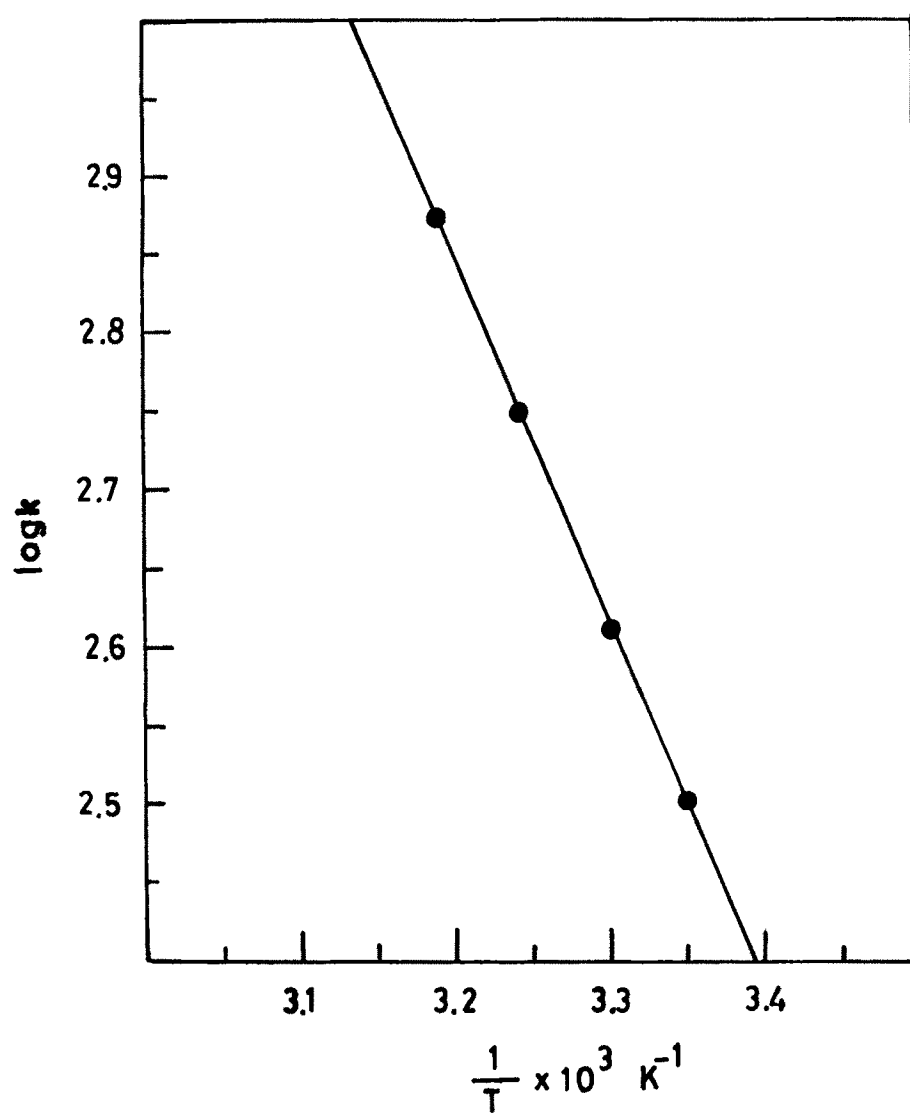


Table V(viii)

Activation parameters of Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium.

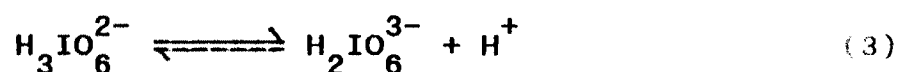
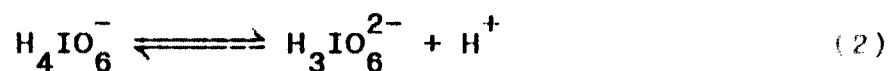
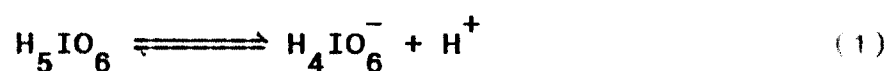
Activation parameters with respect to slow step of the mechanism

Activation parameters	Uncatalysed	Ru(III) Catalyzed
Ea	63.82 ± 3	45.95 ± 2
logA	13.63 ± 0.3	9.70 ± 0.5
ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	$- 96.49 \pm 4$	$- 51.21 \pm 2$
ΔH^\ddagger (kJ mol^{-1})	61.34 ± 3	43.47 ± 2
ΔG^\ddagger (kJ mol^{-1})	90.10 ± 4	58.7 ± 3

Error \pm 5%

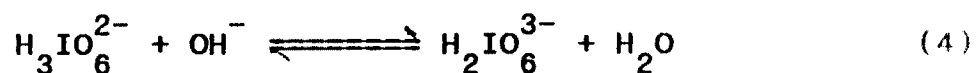
DISCUSSION

The activity of periodate as an oxidizing agent varies as a function of pH. In acid solution, it is one of the most powerful oxidizing agents known, while in alkaline solution, it is slightly less so. However, in aqueous alkaline medium and in the pH range employed in the present study, periodate cannot exist as H_4IO_6^- . Because, in aqueous solution, periodate is involved in equilibria (1) to (3) depending on the pH of the solution.



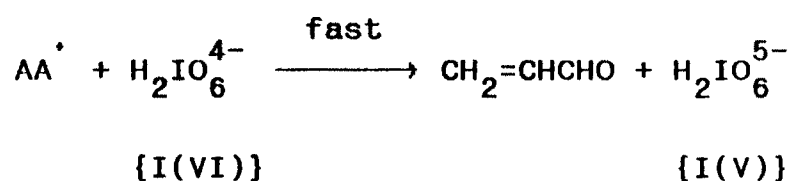
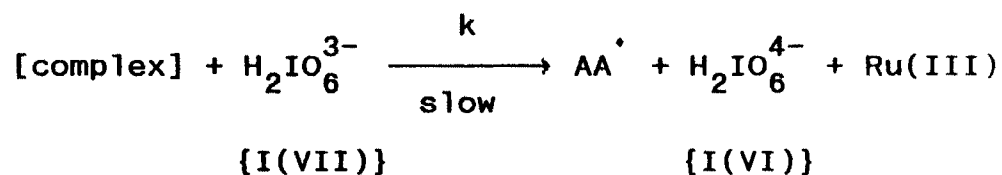
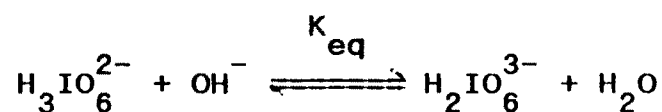
The species H_4IO_6^- exists near pH 7.0. Hence under the alkaline conditions employed in the present, the main species would be expected to be trihydrogen para periodate, $\text{H}_3\text{IO}_6^{2-}$ and dihydrogen para periodate, $\text{H}_2\text{IO}_6^{3-}$. At higher concentrations, periodate can also undergo dimerization. The observed fractional order in [alkali] may be understood in terms of

$\text{H}_2\text{IO}_6^{3-}$ as the main species in alkaline medium with the following equilibria (4).



Increase in rate with $[\text{OH}^-]$ indicates that hydroxylated species of Ru(III) is the active species of the catalyst in the reaction. Since $[\text{OH}^-] \gg [\text{Ru(III)}]$ it is assumed that all Ru(III) is present as hydroxylated species (shown as Ru(III)^* for simplicity). The results suggest the complex formation between the catalyst and substrate, which in turn reacts with alkaline species of oxidant in the rate determining step to give the free radical of allyl alcohol and I(VI) with regeneration of catalyst, Ru(III). As in the case of uncatalysed reaction⁹, the main active species of the oxidant was found to be $\text{H}_3\text{IO}_6^{3-}$. This slow step is subsequently followed by a fast step to yield the final products. Attempts to obtain spectral evidence for such a catalyst-substrate complex were in vain since no appreciable change resulting in the absorption spectra of catalyst or substrate in presence of each other. Furthermore, the plot of $1/k_c$ versus $1/[\text{AA}]$ gave a straight line with an intercept supporting Ru(III)-Allyl Alcohol complex. Such catalyst-substrate complex formation

have been reported earlier¹⁰. Taking all these points into consideration, the mechanism as in scheme 1 may be proposed as follows:



Therefore,

$$\begin{aligned} \text{Rate} &= k [\text{C}] [\text{H}_2\text{IO}_6^{3-}] \\ &= k K [\text{AA}] [\text{Ru(III)}] [\text{H}_2\text{IO}_6^{3-}] \\ &= k K K_{\text{eq}} [\text{AA}] [\text{Ru(III)}] [\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-] \end{aligned} \quad (1)$$

$$[\text{H}_3\text{IO}_6^{2-}]_f = \frac{[\text{H}_3\text{IO}_6^{2-}]}{[1 + K_{\text{eq}} [\text{OH}^-]]} \quad (2)$$

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]}{\{1 + K_{\text{eq}} [\text{H}_3\text{IO}_6^{2-}]\}} \quad (3)$$

$$[\text{Ru(III)}]_f = \frac{[\text{Ru(III)}]}{\{1 + K [\text{AA}]\}} \quad (4)$$

$$[\text{AA}]_f = \frac{[\text{AA}]}{\{1 + K [\text{Ru(III)}]\}} \quad (5)$$

Therefore rate equation becomes

Rate =

$$\frac{k K K_{\text{eq}} [\text{AA}]_T [\text{Ru(III)}]_T [\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-]}{\{1+K_{\text{eq}}[\text{OH}^-]\} \{1+K_{\text{eq}} [\text{H}_3\text{IO}_6^{2-}]\} \{1+K [\text{Ru(III)}]\} \{1+K [\text{AA}]\}} \quad (6)$$

Since $\{1 + K_{\text{eq}} [\text{H}_3\text{IO}_6^{2-}]\}$ and $\{1 + K [\text{Ru(III)}]\}$ is approximately equal to unity

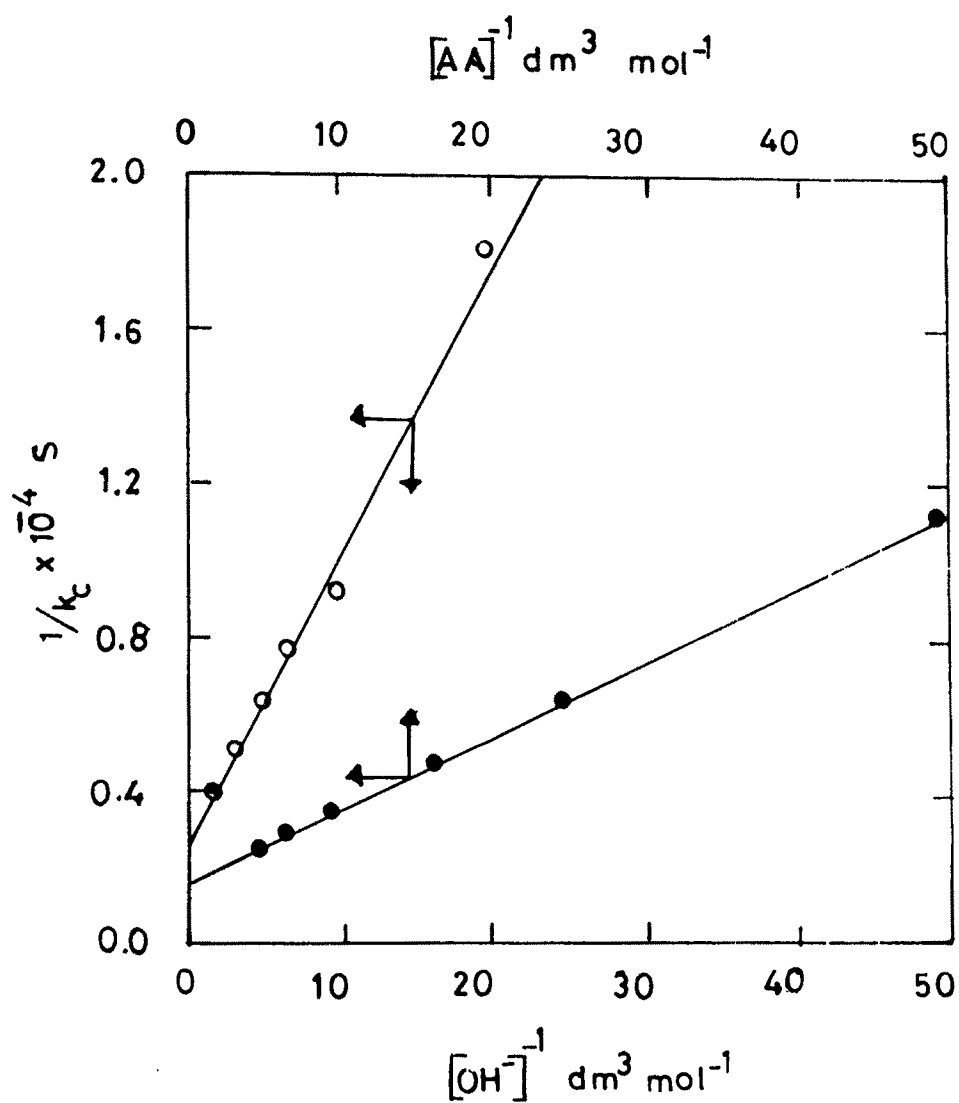
$$\frac{\text{Rate}}{[\text{H}_3\text{IO}_6^{2-}]} = k_c = \frac{k K K_{\text{eq}} [\text{AA}]_T [\text{Ru(III)}]_T [\text{OH}^-]_T}{\{1 + K_{\text{eq}} [\text{OH}^-]\} \{1 + K_3 [\text{AA}]\}} \quad (7)$$

$$\frac{1}{k_c} = \frac{1}{k K K_{eq} [AA] [OH^-] [Ru(III)]} + \frac{1}{k K [AA] [Ru(III)]} + \frac{1}{k K_{eq} [OH^-] [Ru(III)]} + \frac{1}{k [Ru(III)]} \quad (8)$$

The above equation (8) may be verified by plotting $1/k_c$ versus $1/[AA]$ and $1/k_c$ versus $1/[OH^-]$ as shown in Fig.V(iv) (p. 214) at constant concentration of Ru(III). From the slope and intercept of this plot the values of equilibrium constant, K_{eq} , formation constant of the complex between the catalyst and substrate, (K) and rate constant of its decomposition, (k), were evaluated and found to be $3.10 \pm 0.10 \text{ dm}^3 \text{ mol}^{-1}$, $8.23 \pm 0.20 \text{ dm}^3 \text{ mol}^{-1}$ and $3.29 \times 10^2 \pm 0.5 \times 10^1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. Using these values under different experimental conditions it is seen that calculated rate constants were in good agreement with experimental data as shown in the Table V (iii) (p. 197) and Table V(iv) (p. 200).

Figure V(iv)

Verification of rate law: Ru(III) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium
(Conditions as in Table V(iii) (p. 197) and Table V(iv)(p. 200).



The negligible effect of dielectric constant and ionic strength might be due to the involvement of neutral substrate in the reaction.

Findings

In this reaction the main product is acrolein, stoichiometry is 1:1 and initial addition of product have no effect. The reaction shows first order each in [oxidant] and [catalyst] and fractional order dependence both in [substrate] and [alkali]. The main active species of the oxidant, periodate, in alkaline medium is $\text{H}_2\text{IO}_6^{3-}$.

Importance of the results of the Chapter V

It is interesting to note that periodate existing as periodic acid in acid medium, being one of the strongest oxidizing agents in acid medium, oxidation of allyl alcohol in acid medium does not take place even in presence of different catalysts. In acid medium, with different oxidants and catalysts, allyl alcohol gives acrylic acid as the main product whereas in alkaline medium, acrolein is the main product.

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