

## CHAPTER VI

### OSMIUM(VIII) CATALYZED OXIDATION OF ALLYL ALCOHOL BY PERIODATE IN AQUEOUS ALKALINE MEDIUM

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The importance of periodate as an oxidizing agent in acid as well as alkaline medium is given in Chapter V (p. 200). There are numerous reports on the oxidation of organic compounds<sup>1</sup> and also inorganic compounds<sup>2</sup> by periodate.

The emphasis of allyl alcohol in a number of industries is also explained in Chapter IV (p. 147). The oxidation of allyl alcohol by various oxidants has been studied in detail<sup>3</sup>. The importance of Os(VIII) catalyst in organic and inorganic oxidation reactions is given in Chapter IV (p. 148).

We have observed that Os(VIII) catalyzes the oxidation of allyl alcohol by periodate in alkaline medium and details of such study are reported in this chapter to interpret the plausible mechanism.

## EXPERIMENTAL

Reagent grade chemicals and doubly distilled water was used throughout. The preparation of stock solution of Allyl alcohol and Os(VIII) and their standardization is given in Chapter IV (p. 151). Similarly the preparation of periodate and its standardization is explained in Chapter V (p. 189).

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

### *Kinetic Procedure*

Kinetic runs were followed under pseudo-first order conditions at constant temperature  $25.0 \pm 0.1^\circ \text{C}$ . The reaction was initiated by the addition of the allyl alcohol solution containing the required amounts of sodium hydroxide and sodium perchlorate to the periodate solution which also contained Os(VIII) solution of desired concentration. The reaction was followed by measuring the decrease in periodate concentration titrimetrically using sodium thiosulphate solution as

mentioned in the Chapter V (p. 189). Such titrations were carried out at regular intervals of time.

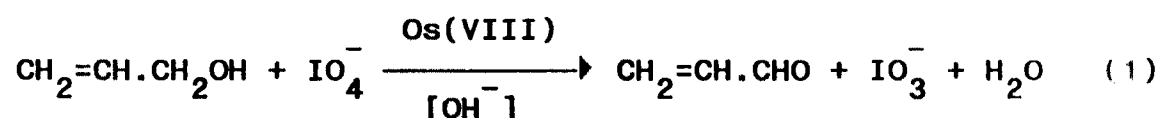
The reaction was generally followed over a period longer than three half-lives. The first order rate constants were obtained from the slope of  $\log[\text{IO}_4^-]$  versus time plots and were reproducible within  $\pm 5\%$  error. The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in a nitrogen atmosphere. No significant difference between the results obtained in presence of nitrogen and in presence of air was noticed.

## RESULTS

### *Stoichiometry*

Various sets of reaction mixtures containing various concentration of periodate and allyl alcohol at constant concentration of sodium hydroxide, sodium perchlorate and osmium(VIII) were allowed to react for 24 h in a closed container at 25°C. As was the case with Ru(III) catalyzed reaction, acrolein was found to be the main product by the spot test<sup>4,5</sup> and test for acrylic acid<sup>6</sup> was negative. The

unreacted periodate, under the condition  $[\text{IO}_4^-] > [\text{AA}]$ , and remaining allyl alcohol, under the condition  $[\text{AA}] > [\text{IO}_4^-]$  were analyzed as mentioned in the Chapter V (p. 194). The product,  $\text{IO}_3^-$  was assayed as given in earlier Chapter V (p. 194). The results showed a consumption ratio of oxidant to reductant as 1:1 (equation 1).



#### REACTION ORDER

Kinetic runs of oxidation of allyl alcohol by periodate in alkaline medium were followed at various initial concentration of oxidant, substrate and alkali in turn keeping all other concentration being constant. With increase of  $[\text{IO}_4^-]$ ,  $[\text{Os(VIII)}]$  and  $[\text{OH}^-]$  showed a positive dependence on the rate of reaction while increase of  $[\text{AA}]$  showed independence of the rate of reaction.

*Effect of Varying [Periodate]*

The periodate concentration was varied in the range  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> at constant concentration of allyl alcohol, alkali, Ru(III) and perchlorate as in Table VI(i) (p. 223). From the plot of  $\log[\text{IO}_4^-]$  versus time shown in Fig.VI(i) (p. 225) the order of the reaction in periodate concentration was unity.

*Effect of Varying [Allyl Alcohol]*

From the linear plot of concentration versus time (Fig.VI(i) p. 225), the order in [AA] was found to <sup>be</sup> zero in the concentration range of  $2.0 \times 10^{-2}$  to  $2.0 \times 10^{-1}$  mol dm<sup>-3</sup> as shown in Table VI(i) (p. 223).

Table VI(1)

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

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

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

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

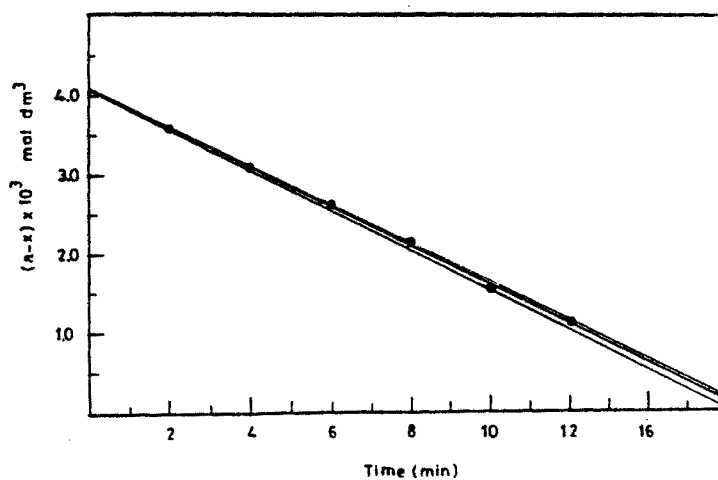
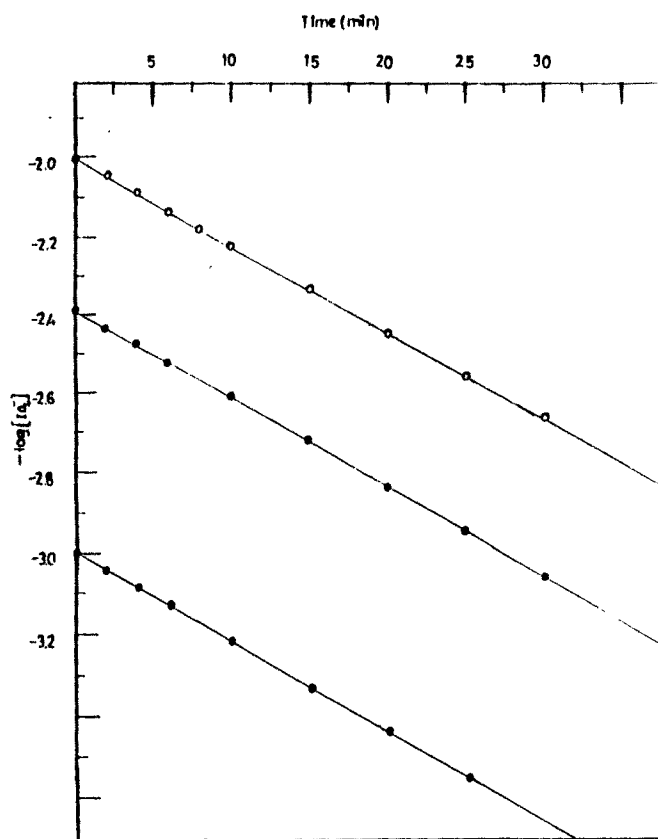
$[\text{IO}_4^-]$ $\times 10^3$ $\text{mol dm}^{-3}$	$[\text{AA}]$ $\times 10^2$ $\text{mol dm}^{-3}$	$k'$ $\times 10^4$ $\text{s}^{-1}$	
		* Expt.	* Calcd.
1.0	4.0	8.52	8.51
2.0	4.0	8.49	8.51
3.0	4.0	8.53	8.51
4.0	4.0	8.50	8.51
6.0	4.0	8.51	8.51
10.0	4.0	8.52	8.51
4.0	2.0	8.51	-
4.0	4.0	8.50	-
4.0	6.0	8.50	-
4.0	10.0	8.51	-
4.0	15.0	8.50	-
4.0	20.0	8.51	-

Error  $\pm 5\%$

\* Experimental and Calculated

Figure VI(1)

First order plot in  $[\text{IO}_4^-]$  and zero order plot in  $[\text{AA}]$ : on  
Os(VIII) catalyzed oxidation of allyl alcohol by periodate  
in aqueous alkaline medium  
(Conditions as in Table VI(i) p. 223)



#### *Effect of Varying [Alkali]*

Keeping all other conditions constant, the alkali concentration was varied in the range of  $5.0 \times 10^{-2}$  to  $5.0 \times 10^{-1}$  mol dm<sup>-3</sup> as given in the Table VI(ii) (p. 226). The order with respect to alkali was found to be less than unity, from the plot of logk' versus log[OH<sup>-</sup>] as shown in the Fig.VI(ii) (p. 227).

#### *Effect of Varying [Catalyst]*

From the plot of logk' versus log[Ru(III)] as shown in the Fig.VI(ii) (p. 227) the order with respect to [Ru(III)] was unity when its concentration was varied in the range  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> as mentioned in the Table VI(ii) (p. 226).



Table VI(ii)

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

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

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

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

$[\text{OH}^-]$ $\times 10$ $\text{mol dm}^{-3}$	$[\text{Os(VIII)}]$ $\times 10^6$ $\text{mol dm}^{-3}$	$k'$ $\times 10^4$ $\text{s}^{-1}$	
		* Expt.	* Calcd.
0.5	5.0	3.10	2.99
1.0	5.0	5.26	5.26
1.5	5.0	6.95	7.06
2.0	5.0	8.50	8.51
3.0	5.0	10.71	10.71
5.0	5.0	13.51	13.51
2.0	1.0	1.70	1.70
2.0	2.0	3.40	3.40
2.0	5.0	8.50	8.51
2.0	6.0	10.20	10.21
2.0	8.0	13.60	13.62
2.0	10.0	17.00	17.00

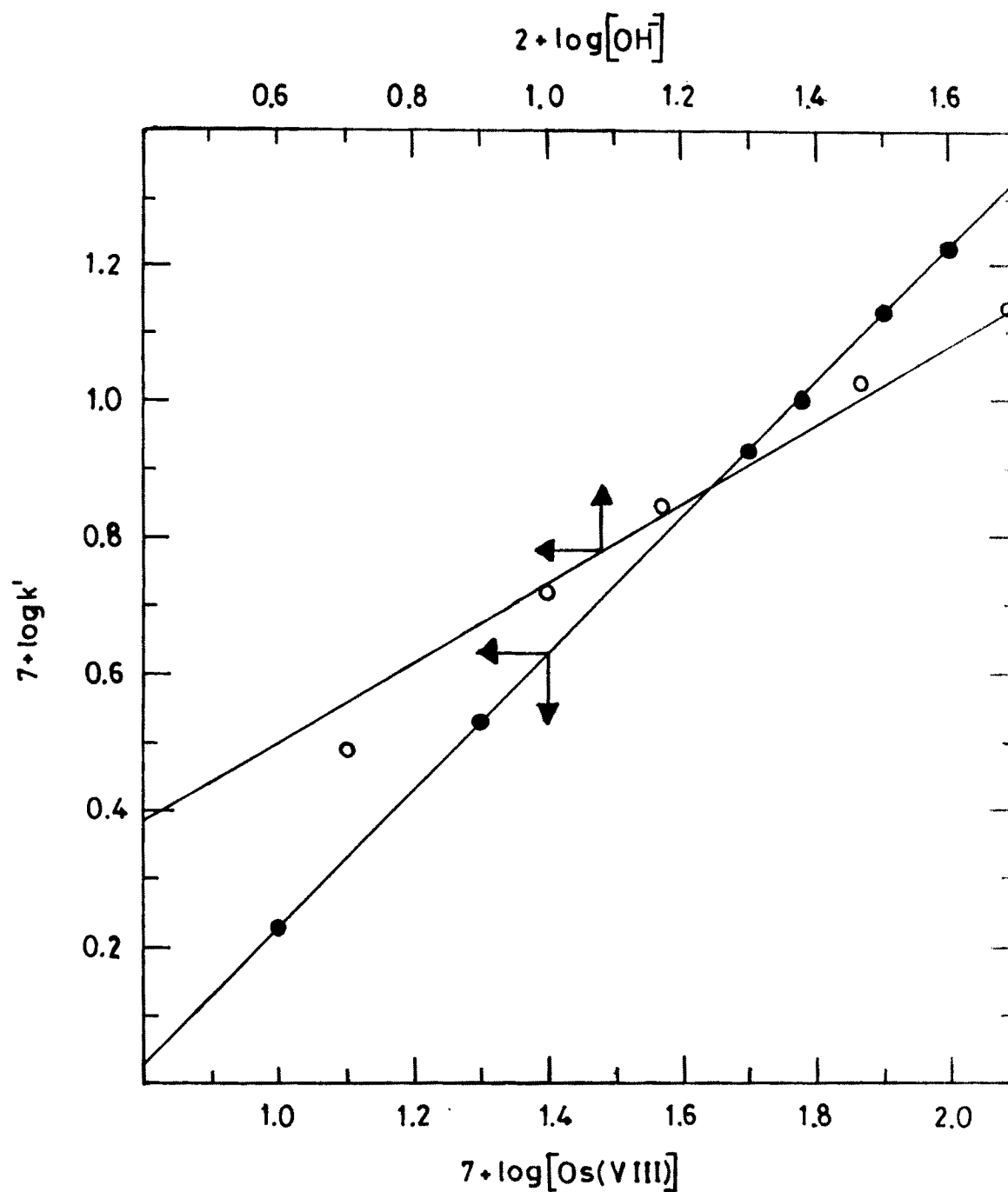
Error  $\pm$  5%

\* Experimental and Calculated

Figure VI(ii)

Order in  $[\text{OH}^-]$  and  $[\text{Os(VIII)}]$ : on Os(VIII) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium

(Conditions as in Table VI(ii) p. 226)



### *Effect of Dielectric Constant*

The effect of Dielectric constant (D) on the reaction medium was studied by using different compositions of t-butanol-water content (v/v) in the reaction mixture, keeping all other conditions constant as given in Table VI(iii) (p. 229). The Dielectric constant of the reaction medium at various percentages of t-butanol and water were calculated as in Chapter I (p. 57). It is noticed that increase in content of t-butanol, from 0.0 to 40.0 % (v/v), did not affect the rate of the reaction to any significant extent as shown in Table VI(iii) (p. 229).

### *Effect of Ionic Strength*

The effect of ionic strength of the reaction medium was studied by carrying out the kinetic runs by varying sodium perchlorate in the concentration range of  $6.0 \times 10^{-2}$  to  $6.0 \times 10^{-1} \text{ mol dm}^{-3}$  with all other conditions being constant as in Table VI(iii) (p.229). It was observed that reaction rate remained almost constant as shown in the Table VI(iii) (p. 229) indicating negligible effect of ionic strength on the rate.

Table VI(iii)

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

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

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

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

$$[\text{Os(VIII)}] = 5.0 \times 10^{-6} / \text{mol dm}^{-3};$$

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

* %	D	k'	I	k'
		$\text{s}^{-1}$	$\text{mol dm}^{-3}$	$\text{s}^{-1}$
0.0	78.5	8.52	0.06	8.49
5.0	75.1	8.50	0.12	8.51
10.0	71.7	8.51	0.20	8.50
20.0	65.0	8.49	0.40	8.52
30.0	58.2	8.50	0.50	8.53
40.0	51.5	8.51	0.60	8.52

\* % = % of t-butanol

### *Effect of Added Products*

Keeping all other conditions constant, the effect of initially added products, iodate and acrolein, each in the concentration range of  $1.0 \times 10^{-3}$  to  $8.0 \times 10^{-3}$  mol dm<sup>-3</sup>, was studied it is found that the rate of reaction was not affected as shown in the Table VI(iv) (p. 231).

### *Test for Free Radicals*

The intervention of 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.

Table VI(iv)

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

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

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

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

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

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

$[\text{IO}_3^-]$ $\times 10^3$ $\text{mol dm}^{-3}$	[Acrolein] $\times 10^3$ $\text{mol dm}^{-3}$	$k'$ $\times 10^4$ $\text{s}^{-1}$
1.0	-	8.51
2.0	-	8.49
4.0	-	8.52
6.0	-	8.50
8.0	-	8.53
-	1.0	8.50
-	2.0	8.53
-	4.0	8.48
-	6.0	8.51
-	8.0	8.52

### *Effect of Temperature*

The rate constants ( $k$ ) of the slow step of the scheme 2 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  $4.44 \times 10^2$ ,  $5.89 \times 10^2$ ,  $7.41 \times 10^2$  and  $9.23 \times 10^2$  at 302, 308, 313 and 318 K respectively. These data were subjected to least square analysis and are tabulated in Table VI(v) (p. 233). From the slope of the plot of  $\log k$  versus  $1/T$  as shown Fig.VI(iii) (p. 234) the activation parameters have been calculated as in Chapter I and are given in Table VI(vi) (p. 235). The activation parameters for uncatalysed reaction are also given in Table VI(vi) (p. 235).

### DISCUSSION

The activity of periodate as an oxidizing agent varies greatly as a function of pH. The nature of periodate ion in aqueous alkaline medium has received considerable attention and the following multiple equilibria of various species depending on the pH of the solution are possible.

Table VI(v)

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

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

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

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

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

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

T	k	1/T (X)	logk (Y)	XY	X <sup>2</sup>	Y <sub>cal.</sub>
	$\times 10^{-2}$	$\times 10^3$		$\times 10^3$	$\times 10^5$	
K	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\text{K}^{-1}$				
298	4.44	3.35	2.64	8.84	1.12	2.63
303	5.89	3.30	2.77	9.14	1.08	2.71
$\Sigma x = 6.65 \times 10^{-3}, \Sigma xy = 17.98 \times 10^{-3}, \Sigma x^2 = 2.2 \times 10^{-5}$						
308	7.41	3.24	2.86	9.26	1.04	2.82
313	9.23	3.19	2.96	9.44	1.01	2.90
$\Sigma x = 6.43 \times 10^{-3}, \Sigma xy = 18.70 \times 10^{-3}, \Sigma x^2 = 2.05 \times 10^{-5}$						

Error  $\pm$  5%



Figure VI(111)

Effect of temperature on Os(VIII) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium  
(Conditions as in Table VI(v) p. 233)

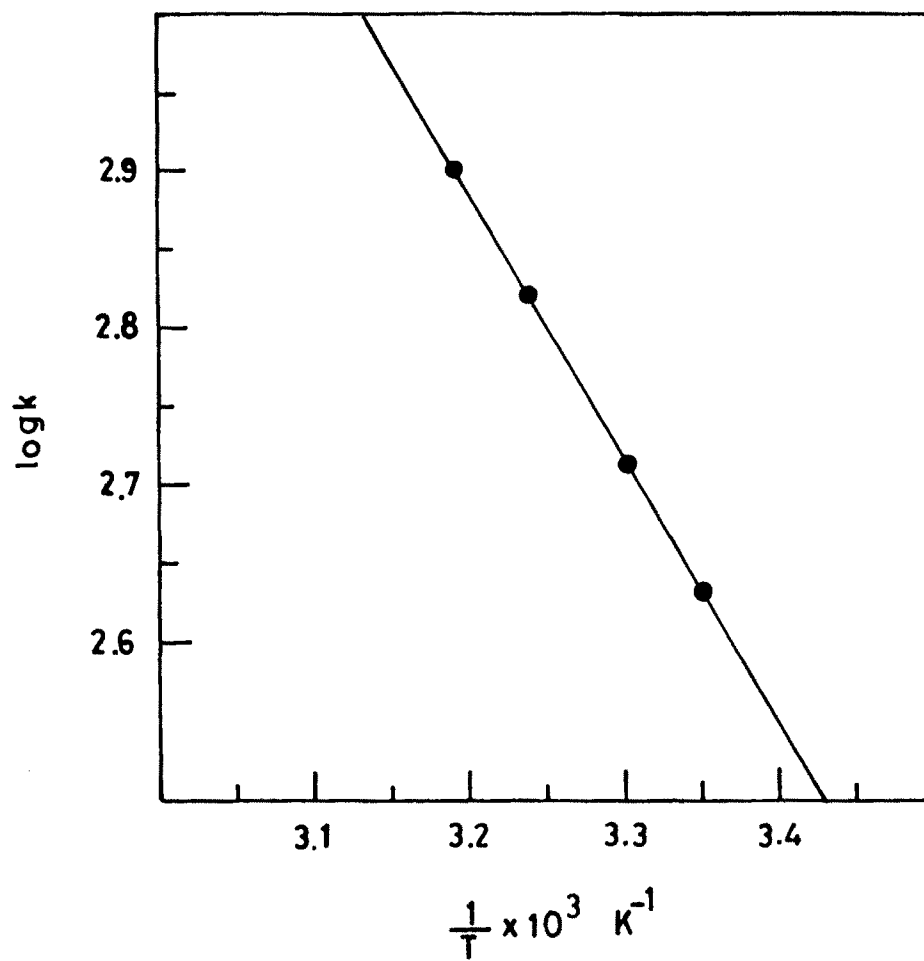
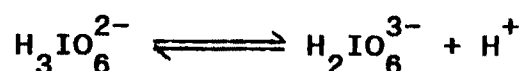
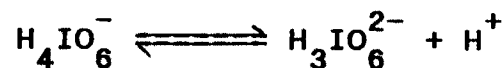
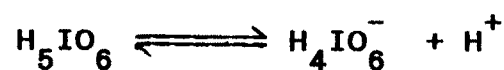


Table VI(vi)

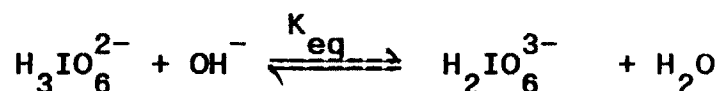
Activation parameters of Os(VIII) catalyzed oxidation of allyl alcohol by periodate in aqueous alkaline medium

Activation parameters with respect to slow step of the mechanism		
Activation parameters	Uncatalysed	Os(VIII) catalyzed
Ea (kJ mol <sup>-1</sup> )	63.82 ± 3	38.29 ± 1.9
logA	13.63 ± 0.6	08.90 ± 0.4
ΔS <sup>#</sup> (J K <sup>-1</sup> mol <sup>-1</sup> )	- 96.49 ± 4	- 74.34 ± 3.5
ΔH <sup>#</sup> (kJ mol <sup>-1</sup> )	61.34 ± 3	35.81 ± 1.7
ΔG <sup>#</sup> (kJ mol <sup>-1</sup> )	90.10 ± 4	57.97 ± 2.5

Error ± 5%



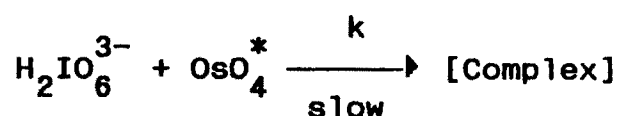
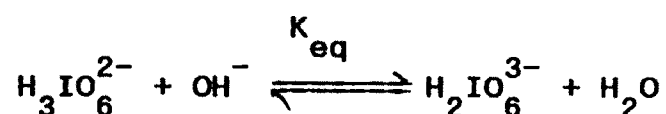
Periodic acid ( $\text{H}_5\text{IO}_6$ ) exists in acid medium<sup>7</sup> and also as  $\text{H}_4\text{IO}_6^-$  around a pH of 7. Thus under the alkaline condition, the main species are expected to be  $\text{H}_3\text{IO}_6^{2-}$  and  $\text{H}_2\text{IO}_6^{3-}$ . The observed fractional order in  $[\text{OH}^-]$ , may be understood in terms of  $\text{H}_2\text{IO}_6^{3-}$  as the main species in alkaline medium with the following equilibrium.



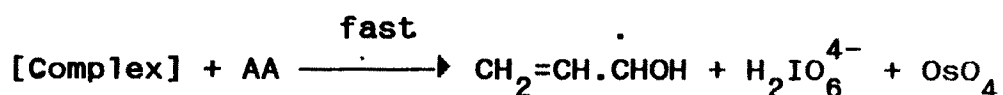
The reaction has 1:1 stoichiometry. Acrolein and  $\text{IO}_3^-$  are the main products of the reaction. The order in  $[\text{IO}_4^-]$  and  $[\text{Os(VIII)}]$  was unity each. While order in  $[\text{OH}^-]$  was less than unity and order with respect to  $[\text{AA}]$  was found to be zero. Since Os(VIII) is known to form different complexes with different  $[\text{OH}^-]$ <sup>8,9</sup> and under the present condition employed in our study, the main active species of Os(VIII) is likely to be

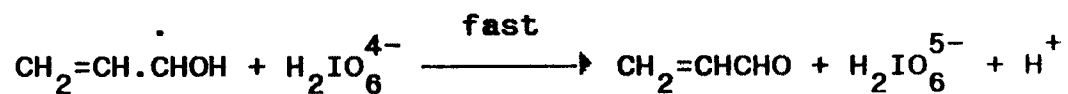
the  $[\text{OsO}_5(\text{OH})]^{3-}$  (shown as  $\text{OsO}_4^*$  in the mechanism for simplicity). The results suggest the complex formation between active species of the oxidant and monohydroxy species of the catalyst in the rate controlling step followed by the subsequent fast steps of interaction of the complex with substrate to give products. No spectral evidence could be obtained for such a complex, since no appreciable change resulting in the absorption spectra of oxidant or catalyst in presence of each other. A feeble interaction is probably involved. such complex formation between catalyst and oxidant have been reported earlier<sup>10</sup>.

Keeping all these points in view, the following scheme may be proposed:



I(VII)





Scheme 1

From Scheme 1,

$$\begin{aligned} \text{Rate} &= k [\text{Os(VIII)}]^* [\text{H}_2\text{IO}_6^{3-}] \\ &= K_{\text{eq}} k [\text{Os(VIII)}]^* [\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-] \end{aligned} \quad (1)$$

$$\begin{aligned} [\text{H}_3\text{IO}_6^{2-}]_{\text{T}} &= [\text{H}_3\text{IO}_6^{2-}]_{\text{f}} + [\text{H}_2\text{IO}_6^{3-}] \\ &= [\text{H}_3\text{IO}_6^{2-}]_{\text{f}} \left\{ 1 + K_{\text{eq}} [\text{OH}^-] \right\} \end{aligned}$$

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

$$\begin{aligned} [\text{OH}^-]_{\text{T}} &= [\text{OH}^-]_{\text{f}} + [\text{H}_2\text{IO}_6^{3-}] \\ &= [\text{OH}^-]_{\text{f}} + K_{\text{eq}} [\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-]_{\text{f}} \\ &= [\text{OH}^-]_{\text{f}} \left\{ 1 + K_{\text{eq}} [\text{H}_3\text{IO}_6^{2-}] \right\} \end{aligned}$$

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

Therefore,

$$\text{Rate} = \frac{k K_{\text{eq}} [\text{Os(VIII)}] [\text{H}_3\text{IO}_6^{2-}]_T [\text{OH}^-]_T}{\left\{ 1 + K_{\text{eq}} [\text{OH}^-] \right\} \left\{ 1 + K_{\text{eq}} [\text{H}_3\text{IO}_6^{2-}] \right\}}$$

$$1 + K_{\text{eq}} [\text{H}_3\text{IO}_6^{2-}] \cong 1$$

$$\text{Rate} = \frac{k K_{\text{eq}} [\text{Os(VIII)}] [\text{H}_3\text{IO}_6^{2-}]_T [\text{OH}^-]_T}{\left\{ 1 + K_{\text{eq}} [\text{OH}^-] \right\}} \quad (4)$$

$$\frac{\text{Rate}}{[\text{Os(VIII)}] [\text{H}_3\text{IO}_6^{2-}]_T} = k' = \frac{k K_{\text{eq}} [\text{OH}^-]_T}{1 + K_{\text{eq}} [\text{OH}^-]} \quad (5)$$

or

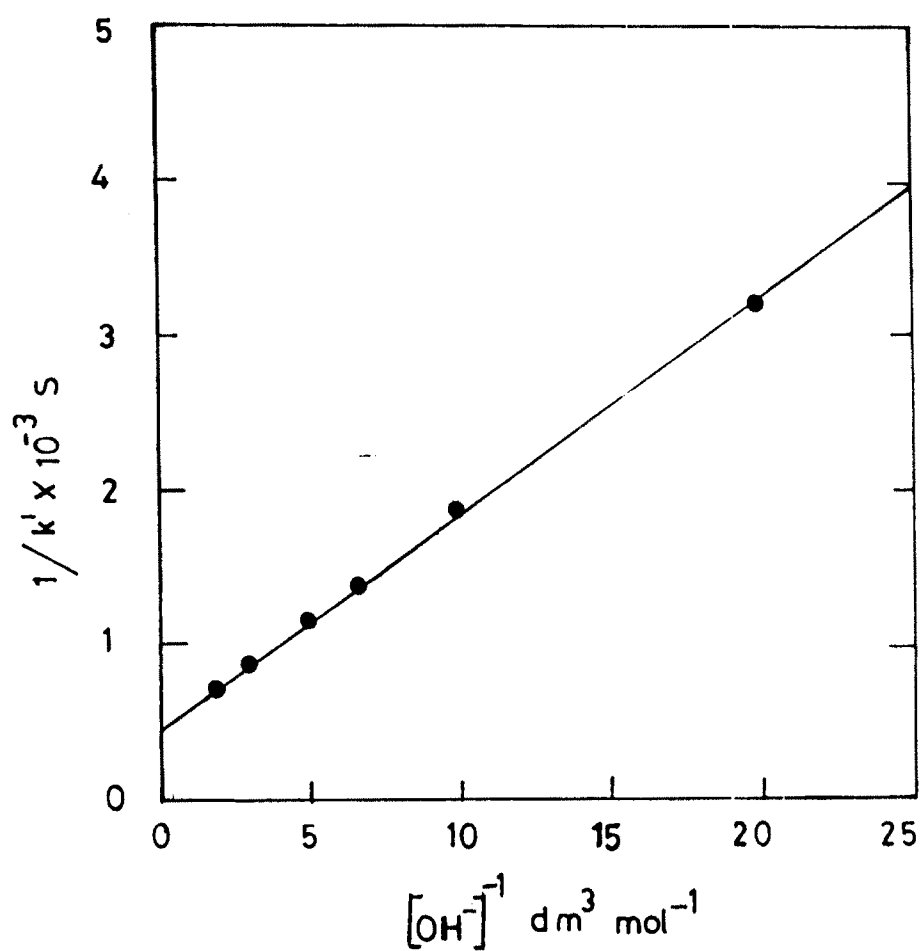
$$\frac{1}{k'} = \frac{1}{k K_{\text{eq}} [\text{OH}^-]_T} + \frac{1}{k}$$

$$\frac{1}{k'} = \frac{1}{k} \left[ \frac{1}{K_{\text{eq}} [\text{OH}^-]} + 1 \right] \quad (6)$$

Finally rate equation (5) may be verified by plotting the graph of  $1/k'$  versus  $1/[\text{OH}^-]$  which is linear as shown in Fig.VI(iv) (p. 241). From the slope and intercept of such plot, the equilibrium constant,  $K_{\text{eq}}$ , as said earlier and rate constant of rate determining step,  $k$  were calculated as  $3.10 \pm 0.1 \text{ dm}^3 \text{ mol}^{-1}$  and  $4.44 \times 10^2 \pm 0.4 \times 10^1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  respectively. Under different experimental conditions these values are utilized to calculate rate constants which were in good agreement with the experimental data (Table VI(ii) p. 226). The value of  $K_{\text{eq}}$  obtained in case of Ru(III) and Os(VIII) catalyzed reaction are nearly agreeable as may be expected since same pre-equilibrium step (1) is involved in the two reaction schemes.

Figure VI(iv)

Verification of rate law: Os(VIII) catalysed oxidation of allyl alcohol by periodate in aqueous alkaline medium  
(Conditions as in Table VI(i) p. 223 and Table VI(ii) p. 226)





## Findings

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

## Importance of the results of the Chapter VI

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 allyl alcohol gives acrylic acid as the main product whereas in alkaline medium acrolein is the main product.

## REFERENCES

1. G. F. Smith and H. Diehl,  
*Talanta*, 4, (1960) 185.  
B. Skalarz, *Quart. Rev. Chem. Soc.*, 3, (1967) 3.
2. R. L. Kaushik and R. Prosad,  
*J. Indian Chem. Soc.*, 46, (1969) 405.
3. S. T. Nandibewoor and J. R. Raju,  
*J. Indian Chem. Soc.*, 55, (1978) 1284.  
K. Ganapathy and C. Karunakaran,  
*Monatsch. Chem.* 113(11), (1982) 1239.  
H. S. Yathirajan, Rangaswamy and Mahadevappa,  
*Collect. Czech. Chem. Commun.*, 47, (1982) 1826.
4. I. L. Uzdina,  
*Hig. Truda.*, 15, (1937) 63.
5. F. Feigl,  
*Spot Tests in Organic Analysis*, Elseveir Publishers,  
(1975) p. 416.

6. G. S. Gokavi and J. R. Raju,  
*Oxid. Commun.*, 11, (1988) 205.
  
7. C. E. Crouthmel, H. V. Meek and D. V. Martin,  
*J. Am. Chem. Soc.*, 73, (1951) 82.  
  
S. M. Tuwar, S. T. Nandibewoor and J. R. Raju,  
*J. Indian Chem. Soc.*, 69, (1992) 651.
  
8. O. C. Saxena,  
*Micro. Chem. J.*, 12, (1967) 609.
  
9. S. M. Tuwar, S. T. Nandibewoor and J. R. Raju,  
*Transition Met. Chem.*, 16, (1991) 335.
  
10. S. T. Nandibewoor and V. A. Morab,  
*J. Chem. Soc. Dalton trans.* (1992) 483.  
  
M. C. Agrawal, R. K. Singhal and S. P. Mushran,  
*Z. Phys. Chem.* 62, (1963) 112.