

CHAPTER IV

OSMIUM(VIII) CATALYZED OXIDATION OF ALLYL ALCOHOL BY N-BROMOSUCCINIMIDE IN AQUEOUS ALKALINE MEDIUM

A large number of N-haloimides (or amides) including some N-fluoro compounds, have since been prepared and tested as reagents for allylic bromination and oxidation of organic compounds. Only a few compounds have been found to have distinct advantages for routine work; others remain of academic interest only. The only reagents which have been found to have as wide acceptability as NBS for allylic bromination are the N-bromohydantoins. However, some of the reagents which were found to be poor allylic brominating reagents have proved to be better reagents in certain other reactions, particularly those involving the use of a polar medium and where the reaction proceeds by an ionic rather than a free radical mechanism. N-Chlorosuccinimide, N-bromoacetamide and N-bromosuccinimide for example, have proved to be stronger oxidants.

N-Bromosuccinimide (NBS) has been extensively used as an

oxidizing agent and analytical reagent especially in acid medium¹. It has been used in the determination several^{2,3} organic compounds; some investigations involving N-Bromosuccinimide oxidation of esters⁴, alcohol^{5,6} and ketones^{7,8} are reported. The studies involving NBS oxidations are extensive in acid medium while that in alkaline medium are scanty.

Allyl alcohol finds a number of industrial applications in the preparation of resins, plasticisers, pharmaceuticals and many organic compounds. Kinetics studies on the oxidation of allyl alcohol with different oxidants such as potassium permanganate, chromic acid, vanadium(V), manganese pyrophosphate, Chloramine-T, Silver(II) etc. have been reported⁹.

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, irridium and ruthenium compounds have been found to act as efficient homogeneous catalysts in numerous redox processes. The genesis of the catalytic activity of the

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. In recent years the use of transition metal ions such as osmium, ruthenium, irridium either alone or as binary mixtures as catalyst¹⁰ 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 been shown¹¹ that metal ions act as a catalyst by one of these different paths like formation of complex with reactants or free radicals etc..

Osmium(VIII) is known to be an efficient catalyst in several redox reactions, particularly in alkaline solution¹² and osmium(VIII) catalysis of a number of organic and inorganic reactions in alkaline medium have been studied¹³.

Csanyi¹³ has suggested that osmium(VIII) can be used as catalyst in acid, neutral and alkaline media. The normal potentials of the Os(VI)/Os(VIII) and Os(IV)/Os(VIII) couples in alkaline medium are 0.30 V and 0.10 V respectively¹⁴.

Hence Os(VIII) may be used as catalyst in alkaline medium. The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed by Agrawal and Upadhyay¹². In general, in osmium(VIII) catalyzed oxidations¹¹, either osmium(VIII) oxidizes directly or via a 1:1 complex with substrate where the role of the oxidant is to regenerate osmium(VIII). OsO_4 is soluble in alkaline solutions. Different equilibria that are possible in alkaline media have been invoked by Mayell¹⁵ and Griffith¹².

Osmium(VIII) catalysis in redox reactions involves several complexities due to the formation of different intermediate complexes, free radicals and different oxidation states of osmium. Osmium tetroxide acts as a catalyst in the oxidation of many organic and inorganic substances¹². Its catalytic action in the oxidation of Sb(III), Cr(III), Sn(II), V(IV), Pb(II), As(III), Se(IV), Te(IV), Ce(III), hydrazine, hydroxylamine, sulphide, sulphite, thiosulphate, tetrathionate, dithionate, thiocyanate, phosphite, hypophosphite, iodine, acetaldehyde, alcohols, maleic acid, fumaric acid, chloroform and phenylhydrazine has been studied. Due to the various intermediates species of osmium(VIII) and

NBS involved, this reaction has been undertaken to learn more about the alkaline redox chemistry of these species.

Furthermore, there is also possibility of complex formation in the reaction. The uncatalysed reaction between NBS and allyl alcohol in aqueous alkaline medium has been reported¹⁶. A micro amount of osmium(VIII) is sufficient to catalyze the reaction in alkaline medium and variety of mechanism are possible. Herein, we report the results of the study of the osmium(VIII) catalyzed oxidation of allyl alcohol by N-bromosuccinimide in aqueous alkaline medium.

EXPERIMENTAL

All the chemicals used were of reagent grade and doubly distilled water was used throughout the work. The stock solution of N-bromosuccinimide (SRL) was prepared in water. The concentration of the solution was verified by titration with standard sodium thiosulphate iodometrically¹⁷, using starch as an indicator.

Allyl alcohol (Koch light) was refluxed¹⁸ with successive quantities of anhydrous potassium carbonate until the carbonate no longer becomes sticky, but remains finely divided

and flows freely. After cooling, the solution was decanted and distilled. The distillate in the range 94-97°C being collected and used to prepare stock solution of allyl alcohol. The stock solution of allyl alcohol was standardized¹⁹ by the addition of excess of chloramine-T, followed by iodometric estimation of the excess.

Sodium thiosulphate (Fischer) was prepared in water. It was standardized²⁰ against potassium iodate as follows: to the potassium iodate solution containing 1.0 mol dm^{-3} sulphuric acid in iodine flask a known volume of standard potassium iodate solution was added. The liberated iodine was titrated against sodium thiosulphate using starch as an indicator. Potassium chloride which was found to be inactive was used to maintain constant ionic strength and potassium hydroxide (AnalaR) was used to get the required alkalinity.

Succinimide was prepared by known method as follows²¹ :
A known amount of succinic acid is taken into round bottom flask and concentrated ammonia solution was added slowly with cooling and shaking. Most of the acid dissolves forming a clear solution of ammonium succinate. The mixture was heated gently with a free flame and then strongly; the ammonium

succinate commences to decompose with evolution of ammonia and succinimide was collected in the flask. The crude succinimide was recrystallized. Its solution was prepared by dissolving a known amount of succinimide in doubly distilled water. The osmium(VIII) solution were prepared by dissolving a weighed amount of OsO_4 (Johnson Matthey) in 0.5 mol dm^{-3} of NaOH and its concentration was ascertained²² by the addition of excess of standard $\text{Fe}(\text{CN})_6^{4-}$ in 1.0 mol dm^{-3} HCl, followed by the titration of unreacted $\text{Fe}(\text{CN})_6^{4-}$ with standard cerium(IV) using ferroin indicator.

Kinetic Procedure

All kinetic runs were carried out under pseudo-first order conditions at $25 \pm 0.1^\circ\text{C}$ unless otherwise stated. The reaction was initiated by mixing previously thermostatted solutions of N-bromosuccinimide and allyl alcohol which also contained the required quantities of potassium hydroxide, potassium chloride, catalyst osmium(VIII) and doubly distilled water (to keep the total volume constant for all runs) in different stoppered bottles. The first solution contained the required concentrations of substrate (allyl alcohol), potassium hydroxide, potassium chloride and catalyst osmium(VIII), the second solution was that of oxidant, (NBS),

of required concentration. One of the reaction solutions was added to the other. The progress of the reaction was followed by iodometric determination of unreacted NBS as follows²³: 5.0 cm³ of reaction mixture was pipetted out into an iodine flask containing 5.0 cm³ of 5% potassium iodide solution and a required amount of M sulphuric acid was added. The iodine liberated by NBS was titrated against standard sodium thiosulphate solution using starch as an indicator. Such titrations were carried out at regular intervals of time. An example run is shown in Table IV(i) (p. 154). The initial rates were obtained from the slopes of the concentration versus time plots. Most of the kinetic runs were followed to more than 80% completion of the reaction and rates were reproducible within $\pm 5\%$. No effect of dissolved oxygen on the rate of reaction was obtained.

The choice of initial rates were made in view of the retarding product effect on the rate of reaction and failure of data to fit good first-order kinetics equation, that is, the $\log[\text{NBS}]$ versus time plots were linear in the initial stages upto 50% of the reaction.

Table IV(1)

Osmium(VIII) catalyzed oxidation of allyl alcohol by
N-bromosuccinimide in aqueous alkaline medium at 25°C

Example run

$$[\text{NBS}] = 1.0 \times 10^{-3};$$

$$[\text{OH}^-] = 0.01;$$

$$[\text{AA}] = 1.0 \times 10^{-2};$$

$$I = 1.1 \times 10^{-2} / \text{mol dm}^3;$$

Time	Burette Readings	[NBS]
min.	cm ³ (0.001M Na ₂ S ₂ O ₃)	× 10 ⁴ mol dm ⁻³
00.00	9.8	9.8
02.00	9.4	9.4
04.00	8.8	8.8
06.00	8.2	8.2
08.00	8.0	8.0
10.00	7.6	7.6
15.00	6.7	6.7
20.00	5.9	5.9
30.00	4.7	4.7
40.00	3.4	3.4
50.00	2.3	2.3
60.00	2.0	2.0
70.00	1.7	1.7
80.00	1.4	1.4

Error ± 5%

RESULTS

Stoichiometry

Different sets of reaction mixtures containing different concentrations of NBS and allyl alcohol at constant concentrations of potassium hydroxide, potassium chloride and catalyst osmium(VIII) were mixed and kept to react for 24 hours at $25 \pm 1.0^\circ\text{C}$ and then analyzed. The remaining NBS was assayed iodometrically as mentioned earlier. Under the conditions, $[\text{AA}] > [\text{NBS}]$ when the NBS had fully reacted, the unreacted allyl alcohol was estimated²⁴ by addition of an excess of chloramine-T followed by iodometric titration. Acrolein was found to be the product as evidenced by spot test^{25,26} as follows: the product, acrolein, was treated with an aqueous solution of sodium nitroprusside containing piperidine, a blue colour appeared which turns red with alkali. Test for acrylic acid was negative. Another main product, succinimide, was detected by the method reported elsewhere. The results were in agreement with 1:1 stoichiometry (equation 1) as shown in Table IV(ii) (p. 156).

Table IV(11)

Stoichiometry* of osmium(VIII) catalyzed oxidation of allyl alcohol by N-bromosuccinimide in aqueous alkaline medium at 25°C

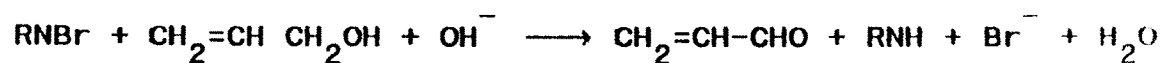
$$[\text{OH}^-] = 0.01$$

$$I = 1.1 \times 10^{-2} / \text{mol dm}^{-3}$$

[NBS] $\times 10^3$ Taken	[AA] $\times 10^3$ Taken	[NBS] $\times 10^3$ Found	[AA] $\times 10^3$ Found
3.00	1.00	2.02	0.00
4.00	2.00	2.05	0.00
5.00	3.00	2.02	0.00
3.00	5.00	0.00	2.06
3.00	6.00	0.00	2.97

Error \pm 5%

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



(1)

where $\text{R} = \text{C}_4\text{H}_4\text{O}_2$

REACTION ORDER

The reaction orders were determined from the slope of log(initial rate) versus log(concentration) plots. The kinetic runs of osmium(VIII) catalyzed oxidation of allyl alcohol by N-Bromosuccinimide in the alkaline medium were followed at different initial concentrations of oxidant, substrate, alkali, osmium(VIII) and potassium chloride in turn while keeping other reactant concentrations constant. With increase in each of [NBS], [AA], [OH⁻] and [Os(VIII)] showed positive dependence on the rate of the reaction. The initial rates were obtained from the concentration versus time curves at the initial stages of the reaction by the plane mirror method and were reproducible to within $\pm 5\%$.

Effect of Varying [N-Bromosuccinimide]

The concentration of NBS was varied in concentration range, 4.0×10^{-4} to 4.0×10^{-3} mol dm⁻³ at fixed [AA], [NaOH] [osmium(VIII)] and ionic strength as in Table IV(iii) (p. 159). The unit slope was obtained from plot of log(rate) versus log(concentration) thus indicating the order in [oxidant] as unity as shown in Fig.IV(i) p. 160).

Effect of Varying [Allyl Alcohol]

The concentration of allyl alcohol was varied in the range 5.0×10^{-3} to 5.0×10^{-2} mol dm⁻³ keeping oxidant, alkali and osmium(VIII) concentrations constant and at constant ionic strength as shown in Table IV(iii) (p. 159). The slope of the plot of log(rate) versus log(concentration) was linear and the order was found to be less than unity from Fig.IV(i) (p. 160).

Table IV(III)

Effects of variation of [NBS] and [AA] on osmium(VIII) catalyzed oxidation of allyl alcohol by N-bromosuccinimide in aqueous alkaline medium at 25°C

$$[\text{OH}^-] = 0.01$$

$$[\text{Os(VIII)}] = 4.0 \times 10^{-6};$$

$$I = 1.1 \times 10^{-2} / \text{mol dm}^{-3};$$

[NBS] $\times 10^3$ mol dm^{-3}	[AA] $\times 10^2$ mol dm^{-3}	Initial rate $\times 10^7$ $\text{mol dm}^{-3} \text{ s}^{-1}$	
		Exptl.*	Calcd.*
0.40	1.00	1.50	1.60
0.70	1.00	2.60	2.80
1.00	1.00	4.12	4.00
1.50	1.00	5.70	6.00
2.00	1.00	7.60	7.99
4.00	1.00	15.10	15.90
1.00	0.50	2.24	2.28
1.00	0.70	3.20	3.02
1.00	1.00	4.12	4.00
1.00	2.00	6.34	6.41
1.00	3.00	8.33	7.96
1.00	5.00	10.00	10.00

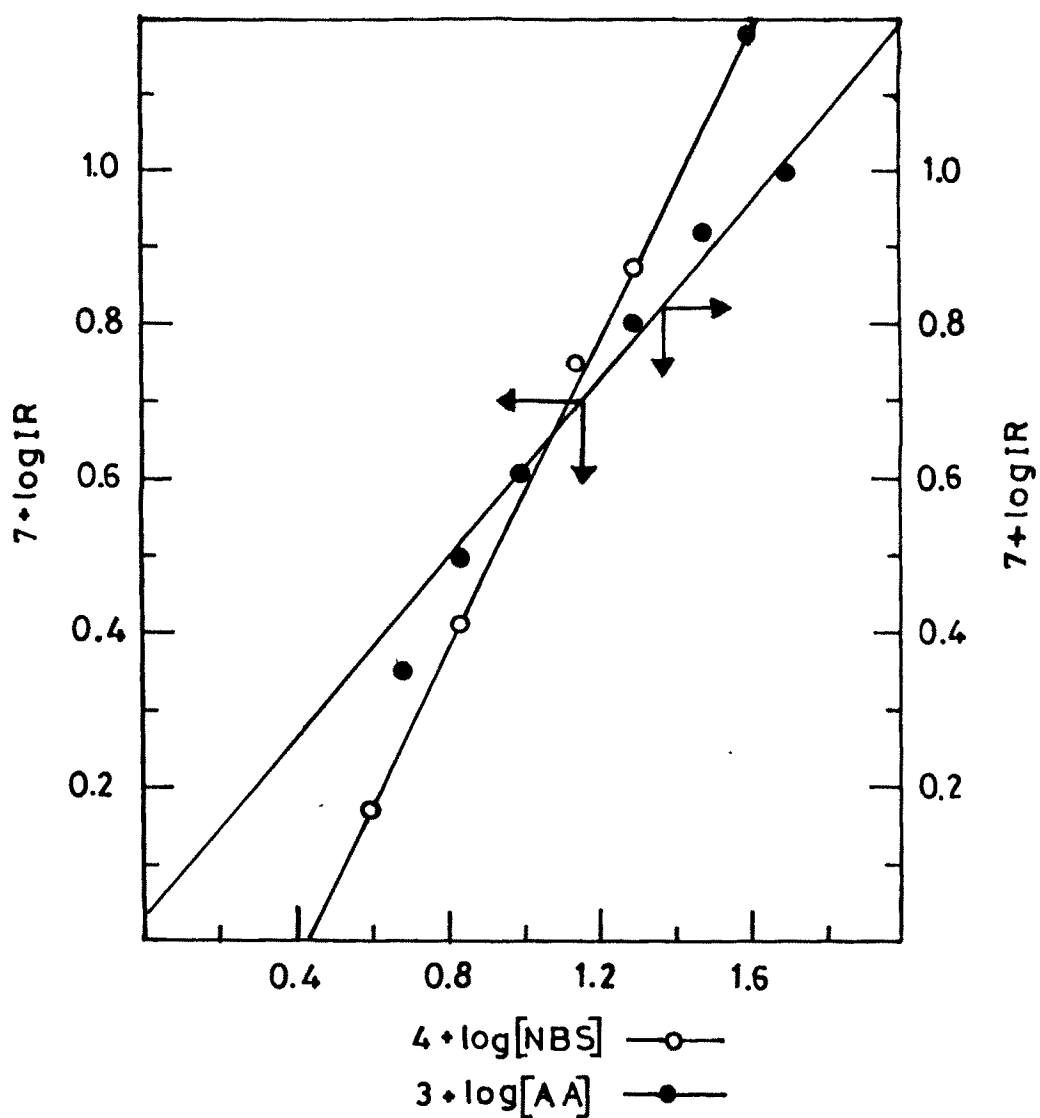
Error \pm 5%

* Experimental and calculated

Figure IV(1)

Order in [NBS] and [AA]: on osmium(VIII) catalyzed oxidation
of allyl alcohol by N-bromosuccinimide in aqueous
alkaline medium

(Conditions as in Table IV(111) p. 159)



Effect of Varying [Alkali]

At constant concentrations of oxidant, reductant, ionic strength and osmium(VIII), the [alkali] was varied in the range 1.0×10^{-3} to 1.0×10^{-2} mol dm⁻³ as given in Table IV(iv) (p. 162). The rate increased with increase in [alkali]. The order in alkali was found by the plot of log(rate) versus log(concentration) and order is obtained as less than unity (Fig.IV(ii) p. 163).

Effect of Varying [Osmium(VIII)]

At constant concentration of oxidant, reductant, alkali, and ionic strength, [Os(VIII)] was varied in the range 8.0×10^{-7} to 8.0×10^{-6} mol dm⁻³ respectively as in Table IV(iv) (p. 162). From log-log plots of initial rate versus concentration, the order with respect to Os(VIII) was found to be unity from Fig.IV(ii) (p. 163).

Table IV(iv)

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

$$[\text{NBS}] = 1.0 \times 10^{-3};$$

$$[\text{AA}] = 1.0 \times 10^{-2};$$

$$I = 1.10^{-2} / \text{mol dm}^{-3};$$

$[\text{OH}^-]$ $\times 10^2$ mol dm^{-3}	$[\text{Os(VIII)}]$ $\times 10^6$ mol dm^{-3}	Initial Rate $\times 10^7$ $\text{mol dm}^{-3} \text{ s}^{-1}$	
		* Exptl.	* Calcd.
0.10	4.00	4.12	4.01
0.20	4.00	4.90	5.04
0.40	4.00	5.60	5.75
0.50	4.00	6.00	5.92
0.70	4.00	6.20	6.11
1.00	4.00	6.24	6.27
1.00	0.80	0.75	0.80
1.00	1.00	0.98	1.00
1.00	2.00	1.88	2.00
1.00	4.00	4.12	4.00
1.00	6.00	5.80	6.00
1.00	8.00	7.70	8.00

Error \pm 5%

* Experimental and calculated

Table IV(v1)

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

$$[\text{NBS}] = 1.0 \times 10^{-3};$$

$$[\text{OH}^-] = 1.0 \times 10^{-2};$$

$$[\text{AA}] = 1.0 \times 10^{-2};$$

$$I = 0.11/\text{mol dm}^{-3};$$

(I)	Initial rate $\times 10^7$ $\text{mol dm}^{-3} \text{ s}^{-1}$	t-Butanol V/V	D	Initial rate $\times 10^7$ $\text{mol dm}^{-3} \text{ s}^{-1}$
0.10	4.20	00.0	78.5	4.25
0.20	4.22	05.0	75.1	4.21
0.30	4.18	10.0	71.7	4.22
0.50	4.21	20.0	65.0	4.18
0.70	4.25	30.0	58.2	4.23
1.10	4.13	40.0	51.5	4.22

Error \pm 5%

Effect of Added Products

Effect of initially added products, succinimide, was studied in the concentration range of 5.0×10^{-4} to 5.0×10^{-3} mol dm⁻³, keeping all other reactants concentrations constant as shown in Table IV(v) (p. 167). It was found that rate decreased with increase in concentration of succinimide. But another product acrolein did not have any significant effect on the rate of reaction as given in the Table IV(v) (p. 167). The initial addition of [Br⁻] has also no significant effect on the reaction rate.

Test For Free Radicals

To test for free radicals, the reaction mixture containing acrylonitrile was kept for 24 hours in an inert atmosphere. Diluting by methanol we did not get any precipitation indicating the absence of free radical intervention in the reaction.

Table IV(v)

Effect of initial addition of products, succinimide and acrolein, on osmium(VIII) catalyzed oxidation allyl alcohol by N-bromosuccinimide in aqueous alkaline medium at 25°C

$$[\text{NBS}] = 1.0 \times 10^{-3};$$

$$[\text{OH}^-] = 1.0 \times 10^{-2};$$

$$[\text{AA}] = 1.0 \times 10^{-2};$$

$$I = 1.10 \times 10^{-2} / \text{mol dm}^{-3};$$

$[\text{NH}]^*$ $\times 10^3$ mol dm^{-3}	$[\text{Acrolein}]$ $\times 10^3$ mol dm^{-3}	Rate $\times 10^7$ $\text{mol dm}^{-3} \text{ s}^{-1}$
0.50	-	4.08
1.00	-	3.63
1.50	-	2.85
2.00	-	2.35
3.00	-	1.81
5.00	-	1.11
-	0.30	4.11
-	0.70	4.09
-	1.00	4.13
-	1.50	4.08
-	2.00	4.14
-	3.00	4.10

Error \pm 5%

* Succinimide

Effect of Temperature

To evaluate the overall activation parameters kinetic runs were studied $\left\{ \begin{array}{l} [\text{NBS}] = 1.0 \times 10^{-3}, \quad [\text{AA}] = 1.0 \times 10^{-2}, \\ [\text{OH}^-] = 1.0 \times 10^{-2}, \quad [\text{Os(VIII)}] = 4.0 \times 10^{-6} \quad \text{and} \quad I = \\ 1.1 \times 10^{-2} / \text{mol dm}^{-3} \end{array} \right\}$ at 298, 303, 308 and 313 K as in Table IV (vii) (p. 169). Increase in initial rate was observed with increase in temperature. From the plot of $\log(\text{initial rate})$ versus $1/T$ (Fig.IV(iii) p. 170) activation parameters were calculated as in Chapter I (p. 62) and are given in Table IV(viii) (p. 171).

DISCUSSION

The reaction is first order each in $[\text{NBS}]$ and $[\text{Os(VIII)}]$ and fractional order both in $[\text{AA}]$ and $[\text{OH}^-]$. The results suggest the complex formation between the catalyst and substrate as platinum group metals have the ability to form complex with organic substrate, highly enhanced rates substantiate the formation of Os(VIII)^* - allyl alcohol complex which slowly reacts with NBS species in the rate determining

Table IV(vii)

Effect of temperature on osmium(VIII) catalyzed oxidation of allyl alcohol by N-bromosuccinimide in aqueous alkaline medium

$$[\text{NBS}] = 1.0 \times 10^{-3}; \quad [\text{AA}] = 1.0 \times 10^{-2};$$

$$[\text{OH}^-] = 1.0 \times 10^{-2}; \quad I = 1.10 \times 10^{-2} / \text{mol dm}^{-3};$$

T^*	IR $\times 10^7$	$1/T(X)$ $\times 10^3$	$\log IR(Y)$	XY	X^2 $\times 10^5$	Y_{cal}^*
K	$\text{mol dm}^{-3} \text{ s}^{-1}$	K^{-1}				
298	4.12	3.35	- 6.38	- 0.021	1.122	- 6.37
303	5.80	3.30	- 6.23	- 0.020	1.089	- 6.24
$\Sigma x = 6.65 \times 10^{-3}, \Sigma xy = - 0.041 \Sigma x^2 = 2.211 \times 10^{-5}$						
308	7.80	3.24	- 6.10	- 0.019	1.049	- 6.09
313	11.40	3.19	- 5.94	- 0.018	1.017	- 5.96
$\Sigma x = 6.43 \times 10^{-3}, \Sigma xy = -0.038, \Sigma x^2 = 2.066 \times 10^{-5}$						

Figure IV(iii)

Effect of temperature on osmium(VIII) catalyzed oxidation of allyl alcohol by N-bromosuccinimide in aqueous alkaline medium
(Conditions as in Table IV(vii) p. 169)

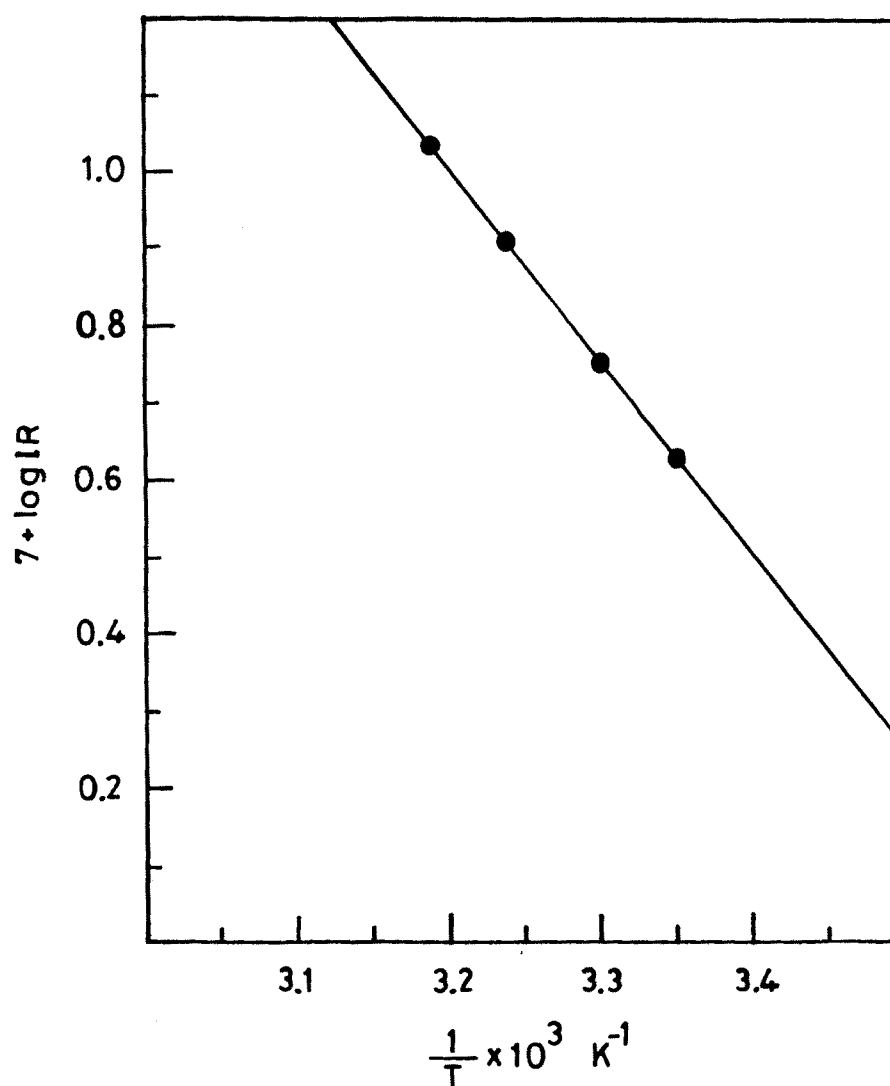


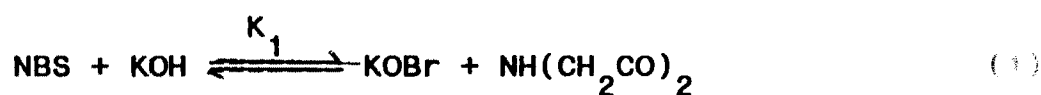
Table IV(viii)

Activation parameters for the osmium(VIII) catalyzed
oxidation of allyl alcohol by N-bromosuccinimide
in aqueous alkaline medium

Activation parameters	Os(VIII) Catalysed
Ea (kJ mol ⁻¹)	76.58 ± 4
logA	11.50 ± 0.50
ΔS [#] (J K ⁻¹ mol ⁻¹)	- 370.84 ± 19
ΔH [#] (kJ mol ⁻¹)	74.04 ± 3
ΔG [#] (kJ mol ⁻¹)	187.32 ± 9

Error ± 5%

step to give products. In alkaline solutions, Os(VIII) is mostly present as hydroxylated species (shown as Os(VIII)* for simplicity) which is in accordance with earlier work^{27,28}. However, it has been known²⁹ that probable reactive species of NBS in acid solutions are >NBr , HOBr , >NHBr , H_2OBr^+ and the reactive species in alkaline solutions are >NBr , HOBr and OBr^- . Taking all these points into consideration a mechanism as in scheme 1 may be proposed.



Scheme 1

Attempts to obtain spectral evidence for catalyst-substrate complex were not successful. However, a kinetic evidence for complex formation can be obtained. Such catalyst-substrate complex formation have been reported earlier^{30,31} Scheme 1 leads to the rate equation (5), as follows:

$$[\text{NBS}]_T = [\text{NBS}]_f + \frac{K_1 [\text{NBS}]_f [\text{OH}_T^- - \text{NH}_f]}{[\text{NH}]_T} \quad (10)$$

$$[\text{NBS}]_T = [\text{NBS}]_f \left\{ 1 + \frac{K [\text{OH}_T^- - \text{NH}_f]}{[\text{NH}]_T} \right\} \quad (11)$$

$$[\text{NBS}]_T = [\text{NBS}]_f \left\{ \frac{[\text{NH}]_T + K [\text{OH}_T^- - \text{NH}_f]}{[\text{NH}]_T} \right\} \quad (12)$$

$$[\text{NBS}]_f = \frac{[\text{NBS}]_T [\text{NH}]_T}{[\text{NH}]_T + K_1 [\text{OH}_T^- - \text{NH}_f]} \quad (13)$$

$$[\text{AA}]_T = [\text{AA}]_f + C$$

$$[\text{AA}]_T = [\text{AA}]_f + K_2 [\text{AA}] [\text{Os(VIII)}]$$

$$[\text{AA}]_T = [\text{AA}]_f \left\{ 1 + K_2 [\text{Os(VIII)}] \right\}$$

$$[\text{AA}]_f = \frac{[\text{AA}]_T}{1 + K_2 [\text{Os(VIII)}]} \quad (14)$$

$$[\text{OH}^-]_f = [\text{OH}_T^- - \text{NH}_f] \quad (15)$$

$$[\text{Os(VIII)}]_{\text{T}} = [\text{Os(VIII)}]_{\text{f}} + \text{C} \quad (16)$$

$$[\text{Os(VIII)}]_{\text{T}} = [\text{Os(VIII)}]_{\text{f}} + K_2 [\text{AA}] [\text{Os(VIII)}] \quad (17)$$

$$[\text{Os(VIII)}]_{\text{T}} = [\text{Os(VIII)}] \left\{ 1 + K_2 [\text{AA}] \right\} \quad (18)$$

$$[\text{Os(VIII)}]_{\text{f}} = \frac{[\text{Os(VIII)}]}{1 + K_2 [\text{AA}]} \quad (19)$$

Substituting the values (13),(14),(15) and (19) in equation (8), we get

$$\begin{aligned} \text{Rate} &= \frac{k K_1 K_2 [\text{NBS}]_{\text{T}} [\text{OH}_{\text{T}}^- - \text{NH}_{\text{f}}] [\text{AA}]_{\text{T}} [\text{Os(VIII)}]_{\text{T}}}{[\text{NH}]_{\text{T}} \left\{ [\text{NH}]_{\text{T}} + K_1 [\text{OH}_{\text{T}}^- - \text{NH}_{\text{f}}] \right\}} \\ &\times \frac{[\text{NH}]_{\text{T}}}{\left\{ 1 + K_2 [\text{AA}] \right\} \left\{ 1 + K_2 [\text{Os(VIII)}] \right\}} \quad (20) \end{aligned}$$

Here $\left\{ 1 + K_2 [\text{Os(VIII)}] \right\}$ is very small compared to unity.

Therefore,

$$\text{Rate} = \frac{k K_1 K_2 [\text{NBS}] [\text{OH}_T^- - \text{NH}_f] [\text{AA}]_T [\text{Os(VIII)}]_T}{\left\{ [\text{NH}]_T + K_1 [\text{OH}_T^- - \text{NH}_f] \right\} \left\{ 1 + K_2 [\text{AA}]_T \right\}} \quad (21)$$

$$\text{Rate} = \frac{k K_1 K_2 [\text{NBS}] [\text{OH}_T^- - \text{NH}_f] [\text{AA}] [\text{Os(VIII)}]}{[\text{NH}] + K_2 [\text{NH}]_T [\text{AA}] + K_1 [\text{OH}_T^- - \text{NH}_f] + K_1 K_2} \\ \times \frac{1}{[\text{OH}_T^- - \text{NH}_f] [\text{AA}]} \quad (22)$$

$$\frac{\text{Rate}}{[\text{NBS}] [\text{Os(VIII)}]} = k_s = \frac{k K_1 K_2 [\text{OH}_T^- - \text{NH}_f] [\text{AA}]}{[\text{NH}]_T + K_2 [\text{NH}]_T [\text{AA}]_T + K_1 [\text{OH}_T^- - \text{NH}_f] + K_1 K_2 [\text{OH}_T^- - \text{NH}_f] [\text{AA}]_T} \quad (23)$$

Here [NH] denotes the product, succinimide, which is in denominator indicates that it retards the rate of reaction. The equation (23) can be rearranged in the form of equation (24)

$$\frac{[\text{NBS}][\text{Os(VIII)}]}{\text{Rate}} = \frac{[\text{NH}]_T}{k K_1 K_2 [\text{OH}_T^- - \text{NH}_T] [\text{AA}]} + \frac{[\text{NH}]_T}{k K_1 [\text{OH}_T^- - \text{NH}_T]} + \frac{1}{k K_2 [\text{AA}]} + \frac{1}{k} \quad (24)$$

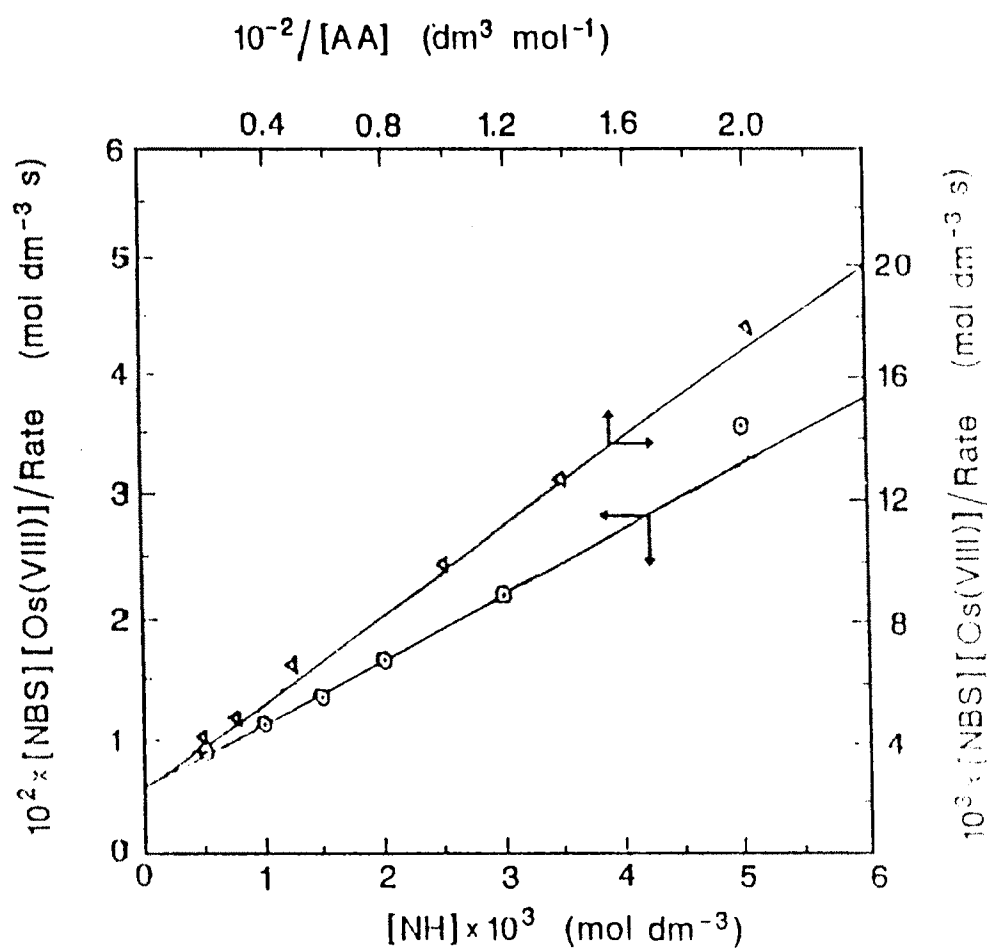
Equation (24) may be verified by the linear plots of $[\text{NBS}][\text{Os(VIII)}]/\text{Initial rate}$ versus $[\text{NH}]$ and $[\text{NBS}][\text{Os(VIII)}]/\text{Initial rate}$ versus $1/[\text{AA}]$ at constant $[\text{Os(VIII)}]$ (Fig. IV(v) p. 178). From the slopes and intercepts of such plots K_1 , K_2 and k were evaluated and found to be $13 \pm 0.6 \times 10^{-2}$, $33.3 \pm 1.5 \text{ dm}^3 \text{ mol}^{-1}$ and $666 \pm 33.3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. Using these values, initial rates can be calculated at different conditions and a good agreement is observed between calculated and experimental rates as shown in Table IV(iii) (p. 159) and in Table IV(iv) (p. 162). The value of K_1 obtained agrees with earlier work³².

Negligible effect of ionic strength and dielectric constant on the reaction might be due to involvement of neutral substrate in the reaction. The activation energy calculated for Os(VIII) catalyzed reaction was found to be

Figure IV(iv)

Verification of rate law: on osmium(VIII) catalyzed oxidation
of allyl alcohol by N-Bromosuccinimide in aqueous alkaline
medium

(Conditions as in Table IV(iii) p. 159 and Table IV(iv) p. 162)



smaller to the uncatalyzed process which explains the catalytic effect²⁹.

Findings

The available data supports that the oxidation of allyl alcohol proceeds through formation of a complex between allyl alcohol and osmium(VIII) which slowly reacts with NBS species in the rate determining step to yield products. One of the main products, succinimide, retards the rate of reaction. The reaction constants involved in the mechanism were derived. The active species of oxidant is found to be OBr^- .

Importance of the results of Chapter IV

The main product of the reaction was found to be succinimide. A mechanism in terms of active species of oxidant and catalyst is proposed and rate law derived. The initial rates were calculated by using the derived constants and are in reasonable agreement with the experimental values.

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