Kinetics of Osmium(VIII) Catalyzed Oxidation of Allyl Alcohol by Potassium Bromate in Aqueous Acidic Medium-Autocatalysis in Catalysis

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ABSTRACT: The kinetics of oxidation of allyl alcohol with potassium bromate in the presence of osmium(VIII) catalyst in aqueous acid medium has been studied under varying conditions. The active species of oxidant and catalyst in the reaction were understood to be Bro_3^- and H_2OsO_5 , respectively. The autocatalysis exhibited by one of the products, that is, Br^- , was attributed to complex formation between bromide and osmium(VIII). A composite scheme and rate law were possible. Some reaction constants involved in the mechanism have been evaluated. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 583–589, 1999

INTRODUCTION

Allyl alcohol finds a number of industrial applications in the preparation of resins, plasticizers, pharmaceuticals and many organic compounds. Kinetic studies on the oxidation of allyl alcohol with different oxidants such as potassium permanganate, chromic acid, vanadium(V), chloramine-T, diperiodatonickelate(IV) and so on have been reported [1–3]. Bromate, Br(V), is known to be a powerful oxidizing agent with redox potentials [4] of 1.44V in acid medium and 0.61V in basic medium. The potentials show that Br₂ in basic solutions can disproportionate spontaneously to BrO⁻ and Br⁻. However, in acidic solutions Br₂ does not disproportionate but, in fact, it accumulates by an autocatalytic reaction. Therefore, in the presence of acid and excess bromide ions, bromate can exclusively act as bromine generator and the resulted bromine can either brominate or oxidize the organic compound under study depending on its nature [5]. Bromate oxidations of organic and inorganic reactions usually involve the complications such as induction period [6] or involvement of two portions [7]. Even bromate oxidations sometimes involve oscillation reactions [8,9]. Hence, the chemistry of bromate ion in aqueous acid medium is of considerable interest due to its importance in mechanistic chemistry [10-17].

Osmium(VIII) acts as a catalyst in the oxidation of many organic and inorganic substrates [18,19] but very few studies are available in acid medium. Os(VIII) catalysis in redox reactions involve different complexities, due to the formation of different inter-

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mediate complexes, free radicals, and different oxidation states of osmium. The oxidation of allyl alcohol by cerium(IV) in aqueous acid medium yielded acrylic acid as the end product. But the use of different catalysts gave different oxidation products [20]. Acrolein is the main product of Os(VIII) catalyzed reaction and acrylic acid is the product for palladium(II) catalyst. In view of various possibilities of mechanism and active species of bromate and osmium(VIII), we have sought to study the title reaction.

EXPERIMENTAL

Materials

Reagent grade chemicals and doubly distilled water were used throughout the experiment. The second distillation of water was from permanganate in a glass still. Stock solution of the oxidant, bromate was prepared by dissolving the potassium bromate (Riedel) in water and the concentration was ascertained [21] by iodometric titration. Bromide was prepared by dissolving a known amount of potassium bromide (BDH). The allyl alcohol (Koch Light) was purified by the reported method [22] and used to prepare the stock solution. It was standardized by addition of an excess chloramine-T, followed by iodometric titration [23]. Osmium(VIII) solution was made by dissolving a known mass of osmium tetroxide(OsO₄)(Johnson Matthey) in 0.50 mol dm⁻³ sodium hydroxide and standardized [24]. Perchloric acid (Merck) and sodium perchlorate were used to provide the required acidity and to maintain the ionic strength, respectively. The stock solutions were used within two days and fresh solutions were used during each kinetic run.

KINETIC STUDIES

The reaction was carried out under pseudo-first-order conditions, where allyl alcohol was always in ten- or more fold excess over the potassium bromate at constant temperature of 27.0 ± 0.1 °C. The reaction was initiated by mixing the previously thermostatted reactant solutions of bromate, allyl alcohol which also contained the required amount of osmium(VIII), sodium perchlorate, perchloric acid, and doubly distilled water (to keep the total volume constant for all runs). Aliquotes (5 ml) of reaction mixture were pipetted out at regular intervals of time and poured into an iodine flask containing 5% of KI and a suitable amount of sulphuric acid. The liberated iodine was titrated against standard sodium thiosulphate solution using starch as an indicator. The rate constants, k_{obs} were obtained from the slopes of the log $[BrO_3^-]$ versus time plots which were linear to about 70% completion of reaction. Most of the kinetic runs were followed to more than 80% completion of the reaction and the rate constants k_{obs} were reproducible within $\pm 5\%$.

RESULTS

Stoichiometry

Different sets of reaction mixtures containing excess concentration of allyl alcohol over bromate in $HClO_4$ at constant ionic strength and with a constant amount of catalyst were kept for 12 hours at 27°C in an inert atmosphere and then analyzed. The remaining allyl alcohol was assayed iodometrically, as mentioned earlier [23]. Acrylic acid formed as the main product was detected by the method [25] and another product bromide was estimated by adding AgNO₃ solution resulting in the formation of precipitate. Test for acrolein was negative [26]. The results proved the consumption ratio of reductant to oxidant as 3 : 2, shown in equation (1).

$$3CH_2 = CH - CH_2 OH + 2KBrO_3 \xrightarrow{HCIO_4} O_{S(VIII)}$$
$$3CH_2 = CH - COOH + 2KBr + 3H_2O$$
(1)

Reaction Order

The order of the reaction was determined from log-log plots of $k_{\rm obs}$ versus concentration at a constant acidity of 0.20 mol dm⁻³ and ionic strength of 0.30 mol dm⁻³. At a fixed concentration of osmium(VIII) of 5.0×10^{-5} mol dm⁻³ the apparent order in [bromate] in the range of 2.0×10^{-4} to 2.0×10^{-3} mol dm⁻³ was unity and the order in [allyl alcohol] in the range 1.0×10^{-2} to 1.0×10^{-1} mol dm⁻³ was unity (Table I). The order in [catalyst] was unity in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm⁻³. With all other reactant concentrations and conditions being constant (Table I), with increasing concentration of acid, the rate decreased (Table I). The uncatalyzed reaction under the given conditions of concentrations is very slow.

Effect of Added Products

Initially added product, acrylic acid did not affect the reaction significantly. However, the initial addition of

$[{\rm BrO_3^{-}}] \times 10^3$ mol dm ⁻³	$[AA] \times 10^2$ mol dm ⁻³	$[\mathrm{H^+}]$ mol dm ⁻³	$\begin{array}{c} [\text{Os(VIII)}] \times 10^5 \\ \text{mol } \text{dm}^{-3} \end{array}$	$k_{ m obs} \mathop{ imes}\limits_{{f S}^{-1}} 10^4$	
				Expt.*	Calcd.*
0.2	4.0	0.20	5.0	3.15	3.27
0.3	4.0	0.20	5.0	3.13	3.27
0.5	4.0	0.20	5.0	3.10	3.27
0.8	4.0	0.20	5.0	3.14	3.27
1.0	4.0	0.20	5.0	3.18	3.27
2.0	4.0	0.20	5.0	3.12	3.27
1.0	1.0	0.20	5.0	0.78	0.80
1.0	2.0	0.20	5.0	1.58	1.63
1.0	4.0	0.20	5.0	3.18	3.27
1.0	6.0	0.20	5.0	5.40	4.91
1.0	8.0	0.20	5.0	7.00	6.60
1.0	10.0	0.20	5.0	8.10	8.20
1.0	4.0	0.02	5.0	6.25	6.22
1.0	4.0	0.03	5.0	5.83	5.92
1.0	4.0	0.05	5.0	5.40	5.41
1.0	4.0	0.10	5.0	4.34	4.44
1.0	4.0	0.15	5.0	3.68	3.70
1.0	4.0	0.20	5.0	3.18	3.27
1.0	4.0	0.20	1.0	0.60	0.65
1.0	4.0	0.20	2.0	1.28	1.30
1.0	4.0	0.20	3.0	1.75	1.96
1.0	4.0	0.20	5.0	3.18	3.27
1.0	4.0	0.20	7.0	5.12	4.60
1.0	4.0	0.20	10	6.80	6.60

Table I Effect of $[BrO_3^{-1}]$, [AA], $[H^+]$, and [Os(VIII)] on Os(VIII) Catalyzed Oxidation of Allyl Alcohol by Bromate in Acid Medium at 300 K; $[Hg(OAc)_2] = 1.0 \times 10^{-2}$ mol dm⁻³, I = 0.30/mol dm⁻³

*Experimental and calculated.

the other product, that is, KBr in the range 1.0×10^{-3} to 1.0×10^{-2} mol dm⁻³, other conditions being constant, increased the rate of reaction with an order of around (0.3). This illustrates the autocatalytic nature of the product (Table II) which is also evident from the concentration versus time plots (Fig. 1) and a linear plot of $k_{\rm expt}$ versus $k_{\rm cal}$ for bromide variation (Fig. 1, Inset).

Effect of Ionic Strength and Solvent Polarity

The effect of ionic strength of the reaction medium was varied from 0.20 to 2.0 mol dm⁻³ with sodium perchlorate at constant concentrations of oxidant, reductant, acid, and catalyst. It was found that ionic strength has negligible effect on the rate of the reaction.

The relative permittivity effect (D) was studied by

varying the acetic acid-water content in the reaction mixture with all other conditions being constant. At-

Table II Effect of Product, $|Br^-|$ on Os(VIII) Catalyzed Oxidation of Allyl Alcohol by BrO_3^- in Acid Medium at 300 K $|AA| = 4.0 \times 10^{-2}$; $|BrO_3^-| = 1.0 \times 10^{-3}$; $|Os(VIII)| = 5.0 \times 10^{-5}$; $|H^+| = 0.20$, I = 0.30/mol dm⁻³

$[Br^{-1} \times 10^{3}]$	$k_{ m obs} \mathop{ imes}\limits_{{ m S}^{-1}} 10^4$		
mol dm ^{-3}	Expt.*	Calcd.*	
1.0	4.12	4.13	
2.0	4.84	4.91	
3.0	5.60	5.57	
5.0	6.40	6.62	
7.0	7.20	7.40	
10	8.40	8.30	

*Experimental and calculated.



Figure 1 Concentration versus time plots. [AA] = 4.0×10^{-2} ; [HBrO₃] = 1.0×10^{-3} ; [H⁺] = 0.20; I = 0.30/mol dm⁻³. (a) [Os(VIII)] = 7.0×10^{-5} mol dm⁻³; (b) [Os(VIII)] = 1.0×10^{-4} mol dm⁻³. Inset: Plot of k_{expt} vs. k'_{cal} = [AA]¹ [Os(VIII)]¹ [H⁺]^{-0.32} [Br⁻]^{0.3} for variation of bromide (Table II).

tempts to measure the relative permittivity of the media were failed. However, they were computed from the values of pure liquids as in earlier work [27–29]. The inertness of the solvent towards oxidant has earlier been tested. It was found that the rate constants k_{obs} increased with decreasing dielectric constant of the medium. The plot of log k_{obs} versus 1/D was linear with positive slope.

Test for Free Radicals

To test for free radicals, the reaction mixture containing acrylonitrile was kept for 24 hours and on dilution with methanol, no precipitate resulted, indicating the absence of free radical intervention in the reaction.

Effect of Temperature

The rate constants were evaluated at four different temperatures and were used for the calculation of activation parameters. The values of k_{obs} (s⁻¹) are 3.18×10^{-4} , 4.92×10^{-4} , 6.55×10^{-4} , and 9.25×10^{-4} at 300, 305, 310, and 315 K, respectively. E_a , $\Delta H^{\#}$, $\Delta G^{\#}$, and $\Delta S^{\#}$ were calculated to be 57.4 \pm 3.0 kJ mol⁻¹, 54.8 \pm 3.0 kJ mol⁻¹, 64 \pm 3 kJ mol⁻¹, and -30.8 ± 2.0 J K⁻¹ mol⁻¹, respectively.

DISCUSSION

The reaction exhibits 2:3 stoichiometry between bromate and allyl alcohol in presence of Os(VIII) catalyst and the orders are found to be unity each in allyl alcohol, bromate and osmium(VIII) concentrations, whereas negative fractional order in [H⁺]. The presence of Mercuric acetate (more than that of bromate concentration) simply means that Br_2 oxidation has been completely suppressed, which otherwise would have formed by interaction of Br^- and bromate as follows

$$BrO_3^- + Br^- + 6 H^+ \Longrightarrow Br_2 + 3 H_2O$$

It is necessary to clarify that in the present study no free radicals were obtained and rates were independent with different concentration of mercuric acetate. These considerations confirm only the complex forming ability of Hg(II) with Br⁻ ion in this reaction. Mercuric acetate acts as a scavenger [30–32] for any Br⁻ formed in the reaction as HgBr₄²⁻ or unionised HgBr₂ and thus ensuring that oxidation takes place purely through bromate. The reported rate constants therefore stand for pure bromate oxidation. At zero [Hg²⁺], the reaction is probably a mixed oxidation by bromate and Br₂.

The important point in bromate oxidations is to establish the reactive species that participates in a given reaction. In acid solution of bromate, the reactive species are likely to be BrO₃⁻ and protonated bromate [HBrO₃ or H_2^+ BrO₃ (BrO⁺₂)]. Hence, the oxidation reaction may be a reaction involving one of the oxidant species. Amis et al. [33] proposed BrO_2^+ as an oxidizing species. Amber and Guttmann [34], Wright and Barton [35], on the other hand, suggested that in moderately strong acid solutions $H_2^+XO_3$ is the existing form of halate ion and in case of bromate, H₂+BrO₃ is the existing form. Beck and co-workers [36], however, have shown that both HBrO₃ and $H_2^+BrO_3$ are the active form of bromate in moderately strong acid solutions. However, in the present study, the decrease of rate with increase in [H⁺] is observed which can be understood due to formation of BrO₃⁻ from HBrO₃ in the prior equilibrium in scheme I. The order of less than unity (negative) in [H⁺] may also be understood in terms of the predominant species of bromate as BrO₃⁻. The orders in oxidant and osmium(VIII) results presumably from a complex formation between the oxidant and catalyst which further reacts with allyl alcohol in a slow step to give the products. Osmium(VIII) is known to form complex [37-39] with other species in view of its vacant d-orbital. The osmium(VIII) species in acid media is understood $\left[40{-}42\right]$ as H_2OsO_5 with very low dissociation constant.

In accordance with the experimental results, the possible mechanism as shown in scheme I is proposed.

$$\begin{split} HBrO_{3} &\stackrel{\kappa_{1}}{\longleftrightarrow} BrO_{3}^{-} + H^{+} \\ BrO_{3}^{-} + H_{2}OsO_{5} &\stackrel{\kappa_{2}}{\longleftrightarrow} Complex (C_{1}) \\ C_{1} + CH_{2} = CH - CH_{2}OH \stackrel{k}{\longleftrightarrow} \\ CH_{2} = CH - CHO + H_{2}OsO_{5} + H_{2}O + BrO_{2}^{-} \\ CH_{2} = CH - CHO + BrO_{2}^{-} \stackrel{fast}{\longleftrightarrow} \\ CH_{2} = CH - COOH + OBr^{-} + H_{2}O \\ CH_{2} = CH - CH_{2}OH + OBr^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - CHO + BrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - CHO + BrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - COOH + BrO_{2}^{-} \\ CH_{2} = CH - CHO + BrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - COOH + BrO_{2}^{-} \\ CH_{2} = CH - CHO + OHrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - CHO + OHrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - CHO + OHrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - CHO + OHrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - CHO + OHrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} = CH - CHO_{3}^{-} OH_{3}^{-} OH_{3}$$

The complex (C_1) might have the following structure.

$$\begin{bmatrix} 0 & OH & O \\ \parallel & 0 & \parallel \\ O = OS - O - Br \\ \parallel & OH & \parallel \\ O & OH & O \end{bmatrix}$$

Evidence for the complex formation was obtained from absorption spectra of both Os(VIII) and Os(VIII)and BrO_3^- mixture, which indicate a hypsochromic shift of about 20 nm due to the participation of d-electrons of Os(VIII) species in bonding which clearly supports complex formation. Kinetic evidence for complex formation is also obtained. Such complex formation between the catalyst and oxidant has also been observed in other studies [43,44].

Thus, scheme I leads to the rate law (2)

$$-\frac{d[\text{HBrO}_3]}{dt} = \frac{kK_1K_2[\text{A A}][\text{HBrO}_3][\text{Os}(\text{VIII})]}{[\text{H}^+] + K_1 + K_1K_2[\text{Os}(\text{VIII})]}$$
(2)

In view of low concentration of osmium(VIII) used, the term such as K_1K_2 [Os(VIII)] is negligible compared to [H⁺] and therefore is neglected. Thus, equation (2) becomes (3).

$$\frac{d[\text{HBrO}_3]}{dt} = \frac{kK_1K_2[\text{A A}][\text{HBrO}_3][\text{Os}(\text{VIII})]}{[\text{H}^+] + K_1}$$
(3)

Rate law (3) accommodates all the experimental results except autocatalysis by bromide. The mechanism of scheme I and rate law (3) may be verified by rearranging it in the form of (4).

$$\frac{[\text{AA}] [\text{OS(VIII)}]}{k_{\text{obs}}} = \frac{[\text{H}^+]}{k\text{K}_1\text{K}_2} + \frac{1}{k\text{K}_2}$$
(4)

The plot of [AA] [Os(VIII)]/ k_{obs} vs. [H⁺] is linear, the slope and intercept of which lead to values of K_1 and kK_2 as 0.18 ± 0.01 mol dm⁻³ and 345.7 ± 17.0 dm⁶ mol⁻² s⁻¹, respectively. From these values, rate constants for several experimental conditions may be calculated from equation (3) and compared with experimentally found data. Such a comparison is made in Table I and shows good agreement between the calculated and experimental rate constants, which fortifies the proposed scheme I.

The ionic strength has negligible effect on the rate of reaction which is in the right direction, since an ion and a neutral molecule are involved [45] in scheme I. However, increase in the content of acetic acid in the reaction medium leads to the increase in the reaction rate, contrary to the expected slower reaction between dipole and a negative ion in the media of lower relative permittivity. This might be due to the solvation of complex in low relative permittivity media [46]. Hence, the net increase in rate with increase in acetic acid content in the medium.

In order to understand the role of metal in binding with the olefinic double bond and its impact on oxidation, the corresponding saturated alcohol, n-propanol, was oxidized by bromate under identical conditions, and did not show any appreciable oxidation even after the period of 24 hours. This indicates that binding of the metal with the olefinic double bond in allyl alcohol is of crucial importance in the oxidation of this substrate which might reduce the energy of activation of reaction path. A similar role of the olefinic bond has been observed in the case of oxidation of allyl alcohol with Ce(IV) [47,48].

The autocatalysis by one of the products, bromide, is interesting. The apparent order of less than unity in bromide concentration when bromide is initially present, may be attributed to complex formation between osmium(VIII) and bromide. The complex (C_2) is then subsequently involved in the interaction with bromate. These steps shown in scheme II will form part of scheme I.

$$\begin{split} H_{2}OsO_{5} + Br^{-} &\stackrel{K_{3}}{\longleftrightarrow} Complex (C_{2}) \\ C_{2} + HBrO_{3} \stackrel{k_{1}}{\longrightarrow} 2BrO_{2}^{-} + H_{2}OsO_{4} + H^{+} \\ BrO_{2}^{-} + H_{2}OsO_{4} \stackrel{fast}{\longrightarrow} H_{2}OsO_{5} + OBr^{-} \\ CH_{2} &= CH - CH_{2}OH + OBr^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + BrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + BrO_{3}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + BrO_{2}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + BrO_{2}^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} \stackrel{fast}{\longrightarrow} \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + OBr^{-} + H_{2}O \\ CH_{2} &= CH - CHO + Br^{-} \\ CH_{2} &= CH - COOH + Br^$$

The structure of the complex (C_2) might be as given below

$$\begin{bmatrix} O \\ \parallel \\ O = Os - Br \\ \parallel \\ O \\ OH \end{bmatrix}$$

The evidence for complex (C_2) formation was also obtained from UV-vis spectra of both Os(VIII) and Os(VIII) and Br⁻ mixture, which indicate a bathochromic shift of about 5 nm and also an increase in intensity for the mixture of Os(VIII) and Br⁻. Indeed, such complex formation between Os(VIII) and Br⁻ have been observed in the literature [49,50]. From scheme II the rate law (5) is obtained.

$$\operatorname{Rate}_{\operatorname{autocat}} = \frac{K_3 k_1 [\operatorname{HBrO}_3] [\operatorname{Os}(\operatorname{VIII})] [\operatorname{Br}^-]}{1 + K_3 [\operatorname{Br}^-]} \quad (5)$$

Thus, when bromide is initially present, a composite scheme involving all the steps of scheme I and II operates and rate law (6a) and then (6b) and (6c) may be derived and rearranged to the form (7).

$$k_{\text{gross}} = \frac{kK_{1}K_{2}[A \ A] \ [Os(VIII)]}{[H^{+}] + K_{1}} + \frac{K_{3}k_{1} \ [Os(VIII)][Br^{-}]}{1 + K_{3}[Br^{-}]} \quad (6a)$$

$$k_{\text{gross}} = k_{\text{cat}} + k_{\text{autocat}}$$
 (6b)
 $k_{\text{gross}} - k_{\text{cat}} = k_{\text{autocat}}$

$$=\frac{K_{3}k_{1} [\text{Os}(\text{VIII})][\text{Br}^{-}]}{1 + K_{3}[\text{Br}^{-}]}$$
(6c)

$$\frac{[\text{Os}(\text{VIII})]}{k_{\text{gross}} - k_{\text{cat}}} = \frac{1}{K_3 k_1 [\text{Br}^-]} + \frac{1}{k_1}$$
(7)

At a constant concentration of oxidant and catalyst, a plot of left hand side of equation (7) vs. 1/[Br⁻] should be linear, and this was found to be so (Fig. 2). Indeed, it is to be noted that the plot shows an intercept which is in agreement with the complex formation as in scheme II. From the slope and intercept, the values of K_3 and k_1 are obtained as $105 \pm 5 \text{ dm}^3 \text{ mol}^{-1}$ and $20 \pm 1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. Using these values the experimental rate constants can be regenerated (Table II).

CONCLUSION

The osmium(VIII) catalyzed bromate oxidation of allyl alcohol, which involves the autocatalytic nature has been studied and the overall mechanistic sequence described here is consistent with product studies, mechanistic studies, and kinetic studies. We have shown that in the catalyzed reaction, autocatalysis has also taken place and a composite rate law is possible. The



Figure 2 Verification of rate law (6) in the form of (7) (Conditions as in Table II).

acid dissociation constant of HBrO₃ has been obtained with the complex rate law.

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