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Kinetics and Mechanism of Oxidation of Primary Alcohols by Chloramine-T Catalyzed by OsO_4

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The kinetics of osmium tetroxide-catalyzed oxidation of primary alcohols by sodium *N*-chloro-*p*-toluene sulfonamide (chloramine-T) has been studied in NaOH medium (1×10^{-4}–1×10^{-1} *M*) over the temperature range 30–50°C. The reaction follows the rate equation

$$-\frac{d[\text{Chloramine-T}]}{dt} = \frac{k_1 K_1 K_2[\text{Alcohol}][\text{OH}^-][\text{OsO}_4]}{1 + K_1[\text{OH}^-]}.$$

The results thus obtained suggest that the oxidation proceeds via formation of an activated complex between the substrate and OsO_4, which slowly decomposes into aldehyde and Os(IV). The Os(IV) thus produced is oxidized rapidly to Os(VIII) with the anion of chloramine-T. The oxidation products are confirmed and a plausible mechanism is proposed.

INTRODUCTION

Chloramine-T is a two electron oxidant in both acidic and basic media (*1*). OsO_4 in alkaline solution is a good catalyst (*2*) for redox reactions. Recently the kinetics of OsO_4 catalyzed oxidation of α-hydroxy acids (*3*), secondary alcohols (*4*), and benzyl alcohol (*5*) by chloramine-T in aqueous solutions containing narrow range of hydroxyl ion concentration have been studied. Hydroxyl ion concentration has significant effect on the kinetics of catalyzed oxidation reaction (*6*). However, the kinetics of oxidation of primary alcohols by chloramine-T in alkaline medium has not been studied. In the present communication, we have reported some results on the oxidation of primary alcohols under a wide range of hydroxyl ion concentrations using OsO_4 as a homogeneous catalyst.

EXPERIMENTAL

E. Merck chloramine-T (CAT) was used. OsO_4 (Johnson Mathey) solution was prepared in NaOH solution. All other chemicals used were A. R. grade. Primary alcohols were fractionated before use. All solutions were prepared using doubly distilled water. The kinetic experiments were followed by adding CAT solutions maintained at a constant temperature (30 ± 0.1°C) to the alcohol solutions containing NaOH and OsO_4 kept in a reaction bottle at the same temperature. The kinetics of the reaction was followed by estimating unreacted CAT using ascorbic acid solution. Initial rates were calculated from the gradients of CAT versus time plots. The detailed experimental procedure has been given elsewhere (*7*).

Stoichiometry. Reaction mixtures containing excess of CAT over alcohols in the presence of NaOH (5×10^{-3} *M*) and OsO_4 (5×10^{-5} *M*) were kept at 30°C for 48 hr. Estimation of unreacted CAT showed the following stoichiometric equation (1)

$$\begin{aligned} &RCH_2OH + CH_3C_6H_4SO_2NClNa \rightarrow \\ &\quad RCHO + NaCl + CH_3C_6H_4SO_2NH_2 \quad (1) \end{aligned}$$

where R = H, CH_3, CH_3CH_2, and $CH_3(CH_2)_2$. Aldehydes were identified from ir spectra. *p*-Toluene sulfonamide was detected by paper chromatography (*8*).

RESULTS

Oxidation of primary alcohols by CAT was carried out at 30°C in the presence of various concentrations (1×10^{-4} to 1×10^{-1}

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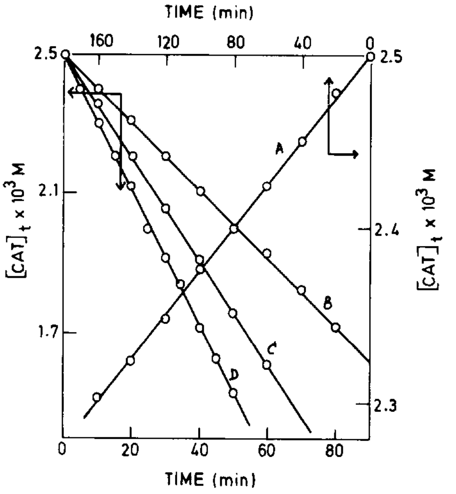

FIG. 1. Reaction feature with respect to CAT. [CAT] = 2.5×10^{-3} M, [Alc] = 0.25 M, [OsO_4] = 5×10^{-5} M, [NaOH] = 5×10^{-3} M. (A) Methanol, (B) ethanol, (C) propanol, and (D) butanol.

M) of NaOH. The reaction of alcohol was found to be very sluggish with CAT in alkaline medium, but the reaction became facile in the presence of traces of OsO_4. Hence, a detailed investigation was made on the kinetics of OsO_4-catalyzed oxidation of primary alcohols by CAT in alkaline medium.

The kinetics of oxidation of primary alcohols by CAT in NaOH (5×10^{-3} *M*) was investigated in the presence of 5×10^{-5} *M* OsO_4 at several initial concentrations (1×10^{-3} to 2.5×10^{-3} *M*) of CAT. From the plots of remaining CAT versus time (Fig. 1), it is clear that the order with respect to CAT is zero. A similar result was obtained at different concentrations of NaOH. The rate of the reaction ($-dc/dt$) was found to be independent of CAT concentration.

The oxidation was also carried out with different concentrations (0.1 to 0.25 *M*) of alcohols in 5×10^{-3} *M* NaOH solution containing 2.5×10^{-3} *M* CAT and 5×10^{-5} *M* OsO_4 at 30°C. An increase in the concentration of alcohol increased the rate of the reaction. Figure 2 shows that the order with respect to the concentration of each alcohol is unity. The reactivity of alcohol is decreased from butanol to methanol.

Kinetic runs were made at several initial concentrations (2.5×10^{-5} to 1×10^{-4} *M*) of OsO_4 in 5×10^{-3} *M* NaOH containing 2.5×10^{-3} *M* CAT and 0.25 *M* alcohol. The rate of

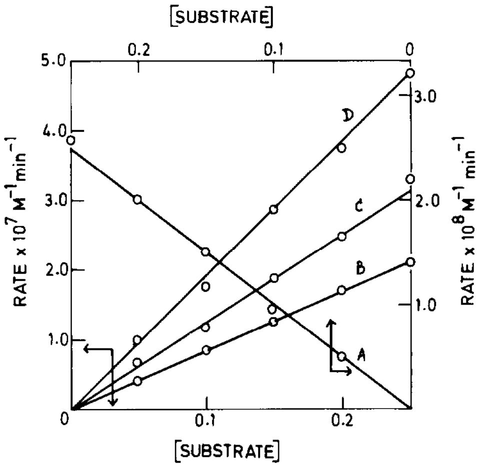

FIG. 2. Effect of variation of alcohol on the reaction rate at 30°C. [CAT] = 2.5×10^{-3} *M*, [NaOH] = 5×10^{-3} *M*, [OsO_4] = 5×10^{-5} *M*. (A) Methanol, (B) ethanol, (C) propanol, and (D) butanol.

TABLE 1

Effect of Variation of OsO_4 Concentration on the Reaction Rate (mol liter^{-1} sec^{-1}) at 30°C[a]

[OsO_4] × 10^5 *M*	BuOH		PrOH		EtOH		MeOH	
	Rate × 10^7	Rate/[OsO_4]	Rate × 10^7	Rate/[OsO_4]	Rate × 10^7	Rate/[OsO_4]	Rate × 10^7	Rate/[OsO_4]
2.5	2.28	91	1.61	64	1.04	42	0.128	5.1
5.0	4.80	96	3.27	65	2.13	46	0.258	5.1
7.5	7.38	91	4.99	66	3.15	46	0.387	5.1
10.0	9.72	97	6.88	68	4.55	45	0.547	5.4

[a] [CAT] = 2.5×10^{-3} *M*; [NaOH] = 5×10^{-3} *M*; [Alc] = 0.25 *M*.

TABLE 2

Effect of Variation of OH^- Ion Concentration on the Reaction Rate at 30°C[a]

$[OH^-] \times 10^{-4}$ *M*	*Rate* $\times 10^8$ (mol liter^{-1} sec^{-1})	Rate $\times 10^4/[OH^-]$	$[OH^-] \times 10^3$ *M*	Rate $\times 10^7$ (mol liter^{-1} sec^{-1})	$[OH^-] \times 10^2$ *M*	Rate $\times 10^7$ (mol liter^{-1} sec^{-1})
1.0	1.80	1.80	1.0	1.70	1.0	7.91
2.5	4.47	1.79	2.5	2.87	2.5	8.01
5.0	8.71	1.74	5.0	4.76	5.0	8.05
7.5	12.59	1.81	7.5	6.42	7.5	8.02

[a] $[CAT] = 2.5 \times 10^{-3}$ *M*, [Alcohol] = 0.25 *M*, $[OsO_4] = 5 \times 10^{-5}$ *M*.

the reaction increased with increase in the concentration of OsO_4 (Table 1). The order in OsO_4 concentration was found to be one from a linear plot of log rate versus log $[OsO_4]$.

The reactions were carried out with 2.5×10^{-3} *M* CAT, 0.25 *M* alcohol, and 5×10^{-5} *M* OsO_4 at 30°C in the presence of various concentrations (1×10^{-4} to 1×10^{-1} *M*) of NaOH. The striking feature of the oxidation of alcohols by CAT in presence of OsO_4 was the dependence of rate on the OH^- ion concentration. Table 2 summarizes the results with butanol at different concentrations of NaOH. At lower concentration range (1×10^{-4} to 1×10^{-3} *M*) the reaction follows first-order dependence on OH^- ion concentration. The reaction tends to become zero order at high concentration range (1×10^{-2} to 1×10^{-1} *M*). Plots of 1/rate versus $1/[OH^-]$ (Fig. 3) in the concentration range (1×10^{-3} to 1×10^{-2} *M*) gives straight lines with definite intercepts showing the fractional order dependence on $[OH^-]$.

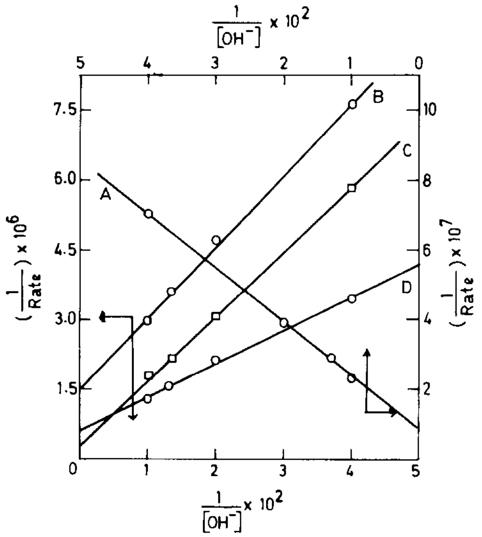

FIG. 3. Plot of $(-dC/dt)^{-1}$ versus $[OH^-]^{-1}$ at 30°C. $[CAT] = 2.5 \times 10^{-3}$ *M*, $[OsO_4] = 5 \times 10^{-5}$ *M*, [Alc] = 0.25 *M*. (A) Methanol, (B) ethanol, (C) propanol, and (D) butanol.

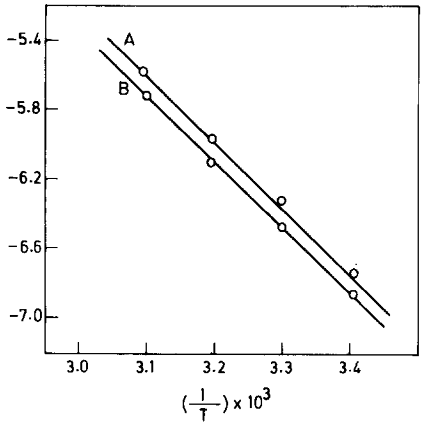

FIG. 4. Plot of log rate versus 1/*T*. $[CAT] = 2.5 \times 10^{-3}$ *M*, $[NaOH] = 5 \times 10^{-3}$ *M*, [Alc] = 0.25 *M*, $[OsO_4] = 5 \times 10^{-5}$ *M*. (A) Butanol, (B) propanol.

Effect of temperature on the rate of oxidation of primary alcohols (0.25 *M*) by CAT (2.5×10^{-3} *M*) in 5×10^{-3} *M* NaOH containing 5×10^{-5} *M* OsO_4 was studied. From the Arrhenius plots (Fig. 4), the activation energies (E^a), the heats of activation ($\Delta H^{\neq}$), and entropies of activation ($\Delta S^{\neq}$)

are calculated (Table 3). Entropy of activation is negative for all the alcohols. Attempt was not made to maintain constant ionic strength during oxidation. However, the effect of change of the ionic strength of the medium ($NaClO_4$, 0.1 to 0.5 M) on reaction rate was found to be negligible in the entire concentration range of NaOH. In order to study the influence of dielectric constant on the rate, oxidation was carried out in the mixture of tertiary butanol and water of various compositions at 30°C. The reaction rate decreased slightly with increase in the composition of tertiary butanol. The plot of log rate versus $1/D$ is linear (butanol, Fig. 5) with a negative slope for each alcohol.

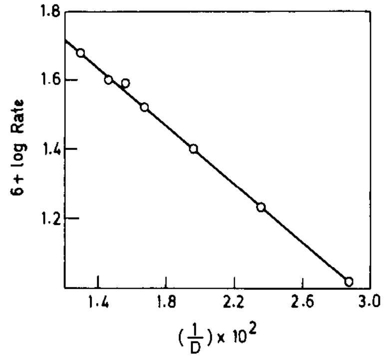

FIG. 5. Plot of log rate versus $1/D$ in tertiary butanol–water at 30°C. [CAT] = $2.5 \times 10^{-3} M$, [Alc] = $0.25 M$, [OsO_4] = $5 \times 10^{-5} M$, [NaOH] = $5 \times 10^{-3} M$.

DISCUSSION

Chloramine-T (RNClNa, where R = $CH_3C_6H_4SO_2$) in aqueous solution gives several oxidizing species (*9*), viz. $RNCl^-$, $RNCl_2$, RNHCl, and OCl^-. The concentration of each species depends on the nature of the medium and pH. In the present system, $RNCl^-$ is the only oxidizing species (*10*). The zero-order in [CAT] indicates that CAT has no role in the formation of the activated complex. OsO_4 in alkaline solution exists in the form of octahedral complexes (*11*) viz. $OsO_4(H_2O)(OH)^{1-}$ and $OsO_4(OH)_2^{2-}$. It is known that $OsO_4(OH)_2^{2-}$ is the only reacting species of the OsO_4 (*12*). Complex formation between the catalyst and the substrate has been reported (*13*).

In the light of these facts, the following probable oxidation mechanism for these alcohols is proposed.

TABLE 3

Thermodynamic Parameters[a]

	E^a (KJ mol^{-1})	$\Delta H^{\neq}$ (KJ mol^{-1})	$\Delta G^{\neq}$ (KJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
BuOH	68.9	66.3	93.2	88.8
PrOH	71.9	69.4	94.3	82.0
EtOH	79.9	77.4	95.3	59.4
MeOH	89.9	87.4	100.7	43.7

[a] [Alcohol] = $0.25 M$, [CAT] = $2.5 \times 10^{-3} M$, [OsO_4] = $5 \times 10^{-5} M$, [NaOH] = $5 \times 10^{-3} M$.

$$OsO_4(H_2O)(OH)^{1-} + (OH)^{1-} \underset{}{\overset{K_1}{\rightleftharpoons}} OsO_4(OH)_2^{2-} + H_2O \quad \text{(I)}$$

$$OsO_4(OH)_2^{2-} + \text{Alcohol} \overset{K_2}{\rightleftharpoons} X \quad \text{(II)}$$

$$X \xrightarrow{k_1} \text{Aldehyde} + OsO_2(OH)_4^{2-} \quad \text{rate-determining step} \quad \text{(III)}$$

$$OsO_2(OH)_4^{2-} + RNCl^- \xrightarrow{\text{Fast}} RNH_2 + OsO_4(OH)_2^{2-} + Cl^- \quad \text{(IV)}$$

This scheme shows that OsO_4 forms the activated complex (X) which disproportionates slowly into products. Assuming

$$[OsO_4] = [OsO_4(OH)^{1-}] + [OsO_4(OH)_2^{2-}] + [X] \quad (1)$$

the final rate law in terms of the decreasing [CAT] takes the form

$$-\frac{d[CAT]}{dt} = \frac{k_1K_1K_2[\text{Alcohol}][OsO_4][OH^-]}{1 + K_1[OH^-]\{1 + K_2[\text{Alcohol}]\}} \quad (2)$$

Since first-order kinetics was obtained with respect to [Alcohol], $1 \gg K_2[\text{Alcohol}]$ and rate Eq. (2) is reduced to

$$-\frac{d[CAT]}{dt} = \frac{k_1K_1K_2[\text{Alcohol}][OH^-][OsO_4]}{1 + K_1[OH^-]} \quad (3)$$

This may be written as

$$\frac{1}{-d[\mathrm{CAT}]/dt} = \frac{1}{k_1K_1K_2[\mathrm{Alcohol}][\mathrm{OH}^-][\mathrm{OsO}_4]} + \frac{1}{k_1K_2[\mathrm{Alcohol}][\mathrm{OsO}_4]} \quad (4)$$

This equation predicts a linearity between 1/rate versus $1/[\mathrm{OH}^-]$ at constant $[\mathrm{OsO}_4]$ and [Alcohol]. This is in accordance with the observed results (Fig. 3). At very low $[\mathrm{OH}^-]$, the inequality $1 \gg K_1[\mathrm{OH}^-]$ is evident and rate Eq. (3) is reduced to

$$-\frac{d[\mathrm{CAT}]}{dt} = k_1K_1K_2[\mathrm{Alcohol}][\mathrm{OsO}_4][\mathrm{OH}^-] \quad (5)$$

This clearly explains the first-order kinetics of the reaction rate with respect to [Alcohol], $[\mathrm{OH}^-]$, $[\mathrm{OsO}_4]$ as well as the zero-order kinetics with respect to [CAT]. At higher $[\mathrm{OH}^-]$, the inequality $K_1[\mathrm{OH}^-] \gg 1$ would dominate and rate Eq. (3) is reduced to

$$-\frac{d[\mathrm{CAT}]}{dt} = k_1K_2[\mathrm{Alcohol}][\mathrm{OsO}_4] \quad (6)$$

This explains the zero-order kinetics with respect to $[\mathrm{OH}^-]$. The values of $k_1K_1K_2$ and k_1K_2 obtained from Eq. (4) for different alcohols are given in Table 4. The close agreement in $k_1K_1K_2$ values by the different methods [from Eqs. (4) and (5)] substantiates the validity of rate Eq. (3) and hence confirms the proposed reaction mechanism. If we compare the $k_1K_1K_2$ values of different alcohols, it can be shown that the rate of oxidation is in the order butanol > propanol > ethanol > methanol. The slight dependence of rate on the dielectric constant (Fig. 5) may be due to the effect of dielectric constant on the preequlibrium steps (I) and (II). The observed neutral salt effect further supports the reaction mechanism.

TABLE 4

Variation of $k_1K_1K_2$ for Different Alcohols at 30°C

Alcohols	$k_1K_1K_2 \times 10^2$ (mol^{-1} liter^{-1} sec^{-1}) (Eq. 4)	$k_1K_1K_2 \times 10^2$ (mol^{-1} liter^{-1} sec^{-1}) (Eq. 5)
Butanol	4.5	6.9
Propanol	2.3	3.4
Ethanol	2.1	2.6
Methanol	2.1	1.2

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