Oxidation of crotyl alcohol by $N$-chloro-4-methylbenzene sulphonamide in acidic medium and in alkaline media in the presence of os(VIII) catalyst-a kinetic pathway

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Abstract: The kinetic pathway of oxidation of crotyl alcohol by sodium salt of $N$-chloro-4-methylbenzene sulphonamide (chloramine-T) in acidic and alkaline medium has been studied. The speciation of chloramine-T has been made to suggest a proper and reasonable reaction mechanism. The thermodynamic quantities such as activation energy and activation entropy are evaluated in acidic as well as in catalysed alkaline medium. An anticipated reaction mechanism has been suggested.

Key words: Electron transfer reaction, reaction kinetics, mechanism, osmium(VIII) catalysis, crotyl alcohol, chloramine-T

1. Introduction

Chloramine-T is a sodium salt of $N$-chloro-4-methylbenzene sulphonamide and this reagent is used as an important antiseptic and disinfectant in chemical analysis [1]. This reagent is not only an important oxidising agent but has also been employed as a chlorinating agent [2]. Apart from this, chloramine-T is considered to be an important analytical reagent in both chemical and pharmaceutical analysis [3] more particularly drugs and syrups.

The unique feature of this reagent is its amide nitrogen being in anion form (negative). Thus the chlorine bound to sulphonamide is positively charged and is, therefore responsible both for oxidation and chlorination [4].

The chemistry of chloramine-T from the view point of kinetics has been extensively studied [5-8] still there are gaps such as the speciation of its species both in acid [9-11] and alkaline [12-14] media which are not yet well defined. Moreover, the reactions of chloramine-T in alkaline medium are comparatively slow and it is this reason that platinum group metal ions [15,16] were considered effective catalysts in this medium.

In most, kinetic studies of oxidation of unsaturated alcohols have been studied in the absence [17] and presence of heterogeneous catalysts [18,19]. Transition metal ions such as Ru(III) [20], Ag(I) [21], Os(VIII) [22], Pd(III) [23] were also taken as homogenous catalysts. But still the product of reactions between unsaturated alcohols and metal ions in solution phase is such an enigma.

As far as the details of oxidation of these alcohols are concerned, a very less amount of information is reported about its kinetic pattern of oxidation of crotyl alcohol by $N$-chloro-4-methylbenzene sulphonamide.

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Since these unsaturated alcohols have been extensively employed in solution with various types of oxidants both metal and nonmetal, yet the details related to the kinetic mechanistic pathway of the reactions apart from identification of oxidation products and dependence of the rate on concentration of hydrogen ion are known to a lesser extent. In view of these observations the title study was undertaken to gain more about the redox chemistry of this important reagent.

2. Results and discussion

2.1. Results

**Part-I: oxidation of crotyl alcohol by chloramine-T in acid aqueous medium** The chloramine-T (CAT) concentration was ranged from $1 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[\text{CA}] = 2 \times 10^{-2}$ mol/dm$^3$; $[\text{H}^+] = 5 \times 10^{-2}$ mol/dm$^3$ at 35 $\pm$ 0.2 C. Initial rates ($k_i$) were analysed by plain mirror method and a graph between initial rate constant ($k_i$) and the oxidant concentration were made that produced a linear line which crossing the origin conformed first order with respect to the CAT. However, pseudo I order graphs were also done (Figure 1) by applying crotyl alcohol and $[\text{H}^+]$ to be $5 \times 10^{-2}$ mol/dm$^3$ at 35 $\pm$ 0.2 C respectively. Pseudo I order rate constants ($k', \text{s}^{-1}$) were independent of oxidant concentrations which was further conforming first order dependence with respect to chloramine-T.

![Figure 1. Pseudo I order plots in oxidation of crotyl alcohol and CAT in acidic medium.](image)

[CA] = $5 \times 10^{-2}$ mol/dm$^3$; [HClO$_4$] = $5 \times 10^{-2}$ mol/dm$^3$

[CAT] = (1) $1.0 \times 10^{-3}$; (2) $1.5 \times 10^{-3}$; (3) $2.0 \times 10^{-3}$; (4) $3.0 \times 10^{-3}$; (5) $5.0 \times 10^{-3}$ mol/dm$^3$ and 35 C

The crotyl alcohol concentration (henceforth written as CA) was ranged from $2.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$ mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$ and $[\text{H}^+] = 5 \times 10^{-2}$ mol/dm$^3$ at 35 $\pm$ 0.2 C. The rate is found to be independent of crotyl alcohol concentration.
P-toluene sulphonamide concentration was ranged from $2 \times 10^{-2}$ to $5 \times 10^{-2}$ mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$; $[\text{H}^+] = 5 \times 10^{-2}$ mol/dm$^3$ at 35 ±0.2 C. The rate was independent of the $p$-toluene sulphonamide concentration. This was also confirmed in variation of crotyl alcohol where the order was zero with respect to crotyl alcohol.

Hydrogen cation effect was studied by applying HClO$_4$ from 0.02 to 0.2 mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$ at 35 ±0.2, 40 ±0.2 and 45 ±0.2 C respectively. The rate was inversely proportional to perchloric acid concentration (Figure 2).

The ionic strength effect was inspected by varying LiClO$_4$ from 0.1 to 1.0 mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$ and $[\text{H}^+] = 5 \times 10^{-2}$ mol/dm$^3$ at 35 ±0.2 C. The rate was independent to ionic strength.

The solvent effect on the reaction rate was inspected by employing $n$-hexane from 5% to 30% (V/V) while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$ and $[\text{H}^+] = 5 \times 10^{-2}$ mol/dm$^3$ at 35 ±0.2 C. The rate was independent of the $n$-hexane concentration.

The temperature effect on the reaction rate was examined at three temperatures i.e. 35 ±0.2, 40 ±0.2, and 45 ±0.2 C, respectively, while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$ and $[\text{H}^+] = 6 \times 10^{-2}$ mol/dm$^3$. The thermodynamic constants i.e. activation energy activation entropy were calculated by applying Eyring calculation made between $T^{-1}$ versus ln k$T^{-1}$ to be (53.84 ±0.31) kJ/mol and (-139.8 ±1.6) J/K mol, respectively.

Free radical test was done on the reaction with acrylic acid [24]. A longer period even after no white sediment was observed in the reaction. This observation eliminates the probability of a free radical in the reaction. However, it might be possible that as soon as a radical is formed, it immediately interacts with the substrate before diffuse out of the solvent cage to interact with the monomer for polymerization [25].

![Figure 2. Variation of hydrogen ion in oxidation of crotyl alcohol and CAT in acidic medium.](image-url)
Part-II: os(VIII) catalysed oxidation of crotyl alcohol by chloramine-T

The chloramine-T concentration was ranged from $2 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[CA] = 5 \times 10^{-2}$ mol/dm$^3$, $[OH^-] = 1 \times 10^{-2}$ mol/dm$^3$ and $[Os(VIII)] = 5 \times 10^{-5}$ mol/dm$^3$ at 45 ± 0.2°C. Since pseudo I order conditions were maintained and thus pseudo I order graphs were made (Figure 3). The pseudo I order rate constants calculated from such graphs were independent of chloramine-T concentrations ensuring first order with respect to chloramine-T.

![Figure 3](image-url)

**Figure 3.** Pseudo I order plots in os(VIII) catalysed reaction in alkaline medium.

$[CA] = 5 \times 10^{-2}$ mol/dm$^3$; $[OH^-] = 1 \times 10^{-2}$ mol/dm$^3$; $[Os(VIII)] = 5 \times 10^{-5}$ mol/dm$^3$  
$[CAT] = (1)$ ◆ $1.0 \times 10^{-3}$; (2) ■ $1.5 \times 10^{-3}$ (3) ▲ $2.0 \times 10^{-3}$; (4) × $2.5 \times 10^{-3}$  
(5) $3.0 \times 10^{-3}$; (6) • $3.5 \times 10^{-3}$ (7) + $4.0 \times 10^{-3}$;  
(8) $4.5 \times 10^{-3}$  
(9) $5.0 \times 10^{-3}$ mol/dm$^3$ and 45°C

The crotyl alcohol concentration was ranged from $1 \times 10^{-3}$ to $5 \times 10^{-2}$ mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[CAT] = 2 \times 10^{-3}$ mol/dm$^3$; $[Os(VIII)] = 5 \times 10^{-5}$ mol/dm$^3$ and constant concentrations of $[OH^-] = 0.005, 0.01$ and $0.02$ mol/dm$^3$, respectively at 45 ± 0.2°C. Initial rates were found to increase initially and then inclined towards a delimit rate at higher alcohol concentrations. Such a dependence of crotyl alcohol appears to be complex. The dependence of crotyl alcohol can be accounted for the Eq. (1) empirically as follows:

$$\frac{d[CAT]}{dt} = \frac{A[CAT][Crotyl\ Alcohol]}{B + C[Crotyl\ Alcohol]} \quad (1)$$

Where A, B and C are empirical rate constants. Rate become independent of it concentration at 0.04 to 0.1 mol/dm$^3$, pseudo I order rate constants obtained in this region are in a good agreement with pseudo I order rate constants obtained in case of variation of concentrations of chloramine-T under pseudo I order conditions (Table).

The osmium(VIII) concentration was ranged from $1 \times 10^{-5}$ to $10 \times 10^{-5}$ mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[CAT] = 2 \times 10^{-3}$ mol/dm$^3$; $[CA] = 5 \times 10^{-2}${

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Table. Pseudo first order and second order rate constants in the reaction of crotyl alcohol with chloramine-T in alkaline medium. [OH\(^-\)] = 0.01 mol/dm\(^3\), Temp. = 45 C

| 10\(^3\)[CAT] (mol/dm\(^3\)) | 10\(^2\)[CA] (mol/dm\(^3\)) | 10\(^4\)[Os(VIII)] (mol/dm\(^3\)) | 10\(^4\) (k') (s\(^{-1}\)) | (k) (mol s/ dm\(^3\)) |
|-----------------------------|-----------------------------|-------------------------------|--------------------------|--------------------------|
| 1.0                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 1.5                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.5                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 3.0                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 3.5                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 4.0                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 4.5                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 5.0                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 1.0                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 1.5                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 2.5                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 3.0                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 3.5                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 4.0                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 4.5                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 5.0                         | 10                          | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 4.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 4.5                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 5.5                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 6.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 6.5                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 7.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 7.5                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 8.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 10.0                        | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 5.0                         | 1.0                           | 0.698                    | 6.91                     |
| 2.0                         | 5.0                         | 2.0                           | 1.354                    | 6.77                     |
| 2.0                         | 5.0                         | 3.0                           | 2.0                     | 6.7                      |
| 2.0                         | 5.0                         | 4.0                           | 2.75                    | 6.90                     |
| 2.0                         | 5.0                         | 5.0                           | 3.454                    | 6.91                     |
| 2.0                         | 5.0                         | 6.0                           | 4.12                    | 6.90                     |
| 2.0                         | 5.0                         | 8.0                           | 5.373                    | 6.7                      |
| 2.0                         | 5.0                         | 10.0                          | 6.909                   | 6.90                     |

mol/dm\(^3\) and [OH\(^-\)] = 1 \times 10^{-2} \text{ mol/dm}^3 \text{ at } 45 \pm 0.2 \text{ C}. The rate constants graph of pseudo first order were made against the Os(VIII) concentration that produced a linear line which crossing the origin conforms the first order with respect to the catalyst (Figure 4).
The hydroxide ion concentration was ranged from 0.01 to 0.1 mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 2 \times 10^{-2}$ mol/dm$^3$; $[\text{Os(VIII)}] = 5 \times 10^{-5}$ mol/dm$^3$; $[\text{OH}^-] = 1 \times 10^{-2}$ mol/dm$^3$ and 45 C.

The rate decreases with increasing hydroxide ion concentration (Figure 5).

The ionic strength effect was studied by using NaNO$_3$ varying from 0.05 to 1.0 mol/dm$^3$ while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$; $[\text{Os(VIII)}] = 5 \times 10^{-5}$ mol/dm$^3$; $[\text{I}] = 1.0$ mol/dm$^3$ at 45 ±0.2, 45 ±0.2 and 50 ±0.2 C, respectively. The rate remains unaltered with the sodium nitrate concentration.
The temperature effect on the rate was examined at 40 ±0.2, 45 ±0.2 and 50 ±0.2 °C respectively while the concentrations of other components of reaction were kept constant at $[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$; $[\text{OH}^-] = 6 \times 10^{-2}$ mol/dm$^3$ and $[\text{Os(VIII)}] = 5 \times 10^{-5}$ mol/dm$^3$. The thermodynamic quantities i.e. activation energy and activation entropy were analysed by using Eyring calculation made between $T^{-1}$ versus ln $kT^{-1}$ to be $(54.62 \pm 0.06)$ kJ/mol and $(-154.19 \pm 0.31)$ J/K mol, respectively.

Free radical test was done by adding acrylic acid into the reaction mixture even after a longer period no white sediment was observed in the reaction. This negates the probability of participation of a free radical in the reaction. However, it might be possible that as soon as a radical is formed, it immediately interacts with the substrate before diffusing out of the solvent cage.

2.2. Discussion

Part-I: oxidation of crotyl alcohol by chloramine-T in acid aqueous medium

The speciation of $N$-chloro-4-methylbenzene sulphonamide known to be chloramine-T is still a question to be settled satisfactorily both in alkaline and acid media. The sodium salt of $N$-chloro-4-methylbenzene sulphonamide being a strong electrolyte reportedly spectates [26,27] in different forms which are governed by Eqs. (2) to (6).

$$\text{RNClNa} \rightleftharpoons \text{Na}^+ + \text{RNCl}^-$$ (2)

$$\text{H}^+ + \text{RNCl}^- \rightleftharpoons \text{RNHCl}$$ (3)

$$2\text{RNHCl} \rightleftharpoons \text{RNCl}_2 + \text{RNH}_2$$ (4)

$$\text{H}_2\text{O} + \text{RNHCl} \rightleftharpoons \text{HOCl} + \text{RNH}_2$$ (5)

$$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$$ (6)

All such species except OCl$^-$ are present in acidic medium [28–30]. Since the order is one with respect to chloramine-T (CAT) and rate is not affected by one of the product, namely 4-methylbenzene sulphonamide (RNH$_2$), the equilibrium steps (4) and (5) governing RNCl$_2$ and HOCl, respectively, are ruled out. OCl$^-$ species conforms to hydroxide ion catalysis which is contrast to observed dependence of hydroxide ion in the title reaction, and thus OCl$^-$ reactivity is also ruled out. Interaction of chloramine-T and crotyl alcohol in acid medium, if discussions regarding species of chloramine-T as mentioned above are any guide along with calculations made by Bishop and Jennings on decinormal solutions of chloramine-T, the RNHCl concentration is significant as contrast to that of RNCl$^-$ species. Since the order is one with respect to the alcohol and CAT each and rate is decelerated by concentration of hydrogen cation, the subsequent mechanism accounting for such experimental observations can be envisaged.

$$\text{RNHCl} + \text{H}^+ \rightleftharpoons \text{RNH}_2^+ + \text{Cl}^-$$ (7)

$$\text{RNHCl} + \text{CA} \xrightleftharpoons[k_2]{k_1} \text{[Complex]}$$ (8)
\[ [\text{Complex}]_1 \overset{k_3}{\rightleftharpoons} \text{Products} \]  \hspace{1cm} (9)

Employing steady state analysis to intermediate [Complex]_1, the rate law (10) is acquired.

\[ \frac{-d[CAT]}{dt} = \frac{k_1 k_3 K [RNHCl] [CA]}{(k_2 + k_3)(1 + K [H^+])} \]  \hspace{1cm} (10)

Since decomposition of the intermediate complex in step (8) is much faster than the rate in the rate determining step (9) i.e. \( k_2 \gg k_3 \), the rate law (10) is reduced to Eq. (11).

\[ \frac{-d[CAT]}{dt} = \frac{k_1 k_3 K [RNHCl] [CA]}{k_2 (1 + K [H^+] + K [H^+]^2)} \]  \hspace{1cm} (11)

where [RNHCl] and [CA] are the comprehensive concentrations of chloramine-T and alcohol, respectively. Thus, the rate Eq. (11) accounts for all experimental observations successfully. However, RNH\(^+_2\)Cl is the protonated chloramine-T species which is not similar in view of its already studied involvement in other reactions of chloramine-T reactions in acid medium.

The rate law (11) is further deduced to Eq. (12).

\[ k = \frac{-d[CAT]/dt}{[CA][CAT]} = \frac{k_1 k_3 K}{k_2} \left( \frac{1}{(1 + K [H^+])} \right) \]  \hspace{1cm} (12)

where ‘k’ is an observed second order rate constant. A graph of \( k^{-1} \) versus [H\(^+\)] was made from the Eq. (13) obtained on double reciprocal and then on rearrangement.

\[ \frac{1}{k} = \frac{k_2}{k_1 k_3} \left( \frac{1}{(K)} + [H^+] \right) \]  \hspace{1cm} (13)

Such a plot produced a linear line crossing through origin (Figure 6).

‘K’ from the ratio of slope and intercept was calculated to be 11.44 dm\(^3\)/mol at 35 \degree C, 11.70 dm\(^3\)/mol at 40 \degree C and 12.61 dm\(^3\)/mol at 45 \degree C, respectively. The ratio of ‘\( k_2 / k_1 \)’ was calculated from the slope to be 11.59 \times 10^{-2}, 9.45 \times 10^{-2} and 7.87 \times 10^{-2} at 35 \pm 0.2, 40 \pm 0.2 and 45 \pm 0.2 \degree C, respectively. So far, as the manner of transfer of electron from the alcohol to the chloramine-T is considered, hydrogen anion transfer from \( \alpha \)-carbon of alcohol to chloramine-T occurs as represented by the following scheme – 1.

**Part-II: os(VIII) catalysed oxidation of crotyl alcohol by chloramine-T**

The solution is red colour of osmium tetraoxide in strongly alkaline medium [31] is reported due to the formation of \([\text{OsO}_4 (\text{OH})_2]^{2-}\). Such a complex in dilute alkaline medium is converted in to \([\text{OsO}_3 (\text{OH})_3]^-\) as reported by Sandell et al. [32]. Since the rate reduces with increasing concentration of hydroxide ion, all the complexes of Os(VIII) following to \([\text{OsO}_3 (\text{OH})_3]^-\) species should be less reactive. Further, an sharp reddish brown colour of transient life time appeared on adding crotyl alcohol in Os(VIII) solution at ambient temperature (~5 C) whereas no such colour change was observed with either of these reagents on addition into chloramine-T.
Figure 6. A plot of $(k)^{-1}$ versus $[H^+]$ in oxidation of crotyl alcohol and CAT in acidic medium. $[\text{CAT}] = 2 \times 10^{-2}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$; ♦ 35, ■ 40 and ▲ 45 °C

Scheme 1.

solution. The formation of chelate between CAT and Os(VIII) has been documented in oxidation of α-hydroxy acids but no such colour change or chelate formation was indicated in the reference reaction. Therefore, considering experimental considerations, the order is one with respect to [CAT] and [OS(VIII)] each, dependence of complex with respect to crotyl alcohol and inverse hydroxide ion dependence, subsequent mechanism consisting of steps (14) to (18) can be anticipated.

\[
\begin{align*}
\text{OH}^- + [\text{OsO}_3(\text{OH})_3]^- & \rightleftharpoons K_1 \text{H}_2\text{O} + [\text{OsO}_4(\text{OH})_2]^{2-} \quad (14) \\
\text{CA} + [\text{OsO}_3(\text{OH})_3]^- & \rightleftharpoons K_2 [\text{OsO}_4(\text{OH})_2(\text{CA})]^- \quad (15) \\
\text{CA} + [\text{OsO}_4(\text{OH})_2]^{2-} & \rightleftharpoons K_3 [\text{OsO}_4(\text{OH})_2(\text{CA})]^{2-} \quad (16)
\end{align*}
\]
Thus the loss of chloramine-T leads to the rate law (19) or (20).

\[
-\frac{d[\text{CAT}]}{dt} = \frac{[\text{CAT}] [\text{Os (VIII)}] [\text{CA}] (k_1 K_2 + k_2 K_1 K_3 [\text{OH}^{-}])}{1 + K_1 [\text{OH}^{-}] + K_2 [\text{CA}] + K_1 K_3 [\text{OH}^{-}] [\text{CA}]},
\]

where [CAT] and [Os(VIII)] are the comprehensive concentrations of chloramine-T and osmium(VIII), respectively.

Or

\[
k = \frac{[\text{CA}] (k_1 K_2 + k_2 K_1 K_3 [\text{OH}^{-}])}{1 + K_1 [\text{OH}^{-}] + K_2 [\text{CA}] + K_1 K_3 [\text{OH}^{-}] [\text{CA}]},
\]

where ‘k’ is an observed second order rate constant and [CA] is the free equilibrium concentration of crotyl alcohol.

Since limiting rate is not found even at high hydroxide ion concentration, the second term in the numerator is insignificant and can be ignored. This changes the rate law (20) to (21).

\[
k = \frac{k_1 K_2 [\text{CA}]}{1 + K_1 [\text{OH}^{-}] + K_2 [\text{CA}] + K_1 K_3 [\text{OH}^{-}] [\text{CA}]},
\]

A graph of 1/k versus 1/[CA] was done from the double reciprocal plot of Eq. (21), a linear line with nonzero intercept was produced (Figure 7).

**Figure 7.** A plot of 1/k versus 1/[CA] in os(VIII) catalysed reaction in alkaline medium.

\[
[\text{CAT}] = 2 \times 10^{-2} \text{ mol/dm}^3; [\text{Os(VIII)}] = 5 \times 10^{-5} \text{ mol/dm}^3
\]

\[
[\text{OH}^{-}] = \text{●} 5 \times 10^{-3}; \text{■} 1 \times 10^{-2}; \text{▲} 2 \times 10^{-2} \text{ mol/dm}^3 \text{ and 45 °C}
\]
The calculated slope \((S_1)\) and intercept \((I_1)\) from this plot are represented by Eqs. (22) and (23) respectively.

\[
(S_1) = \frac{1 + k_1 [\text{OH}^-]}{k_1 K_2} \tag{22}
\]

\[
(I_1) = \frac{(K_2 + K_1 K_3 [\text{OH}^-])}{k_1 K_2} \tag{23}
\]

Further graphs of \([\text{OH}^-]\) versus \((I_1)\) and \([\text{OH}^-]\) versus \((S_1)\) respectively were also made that obtained linear line crossing through origin (Figures 8 and 9), \(k_1\) and \(K_1\) were calculated from these plots to be \(2.24 \times 10^{-2}\) dm\(^3\)/mol s\(^{-1}\) and 47.6 dm\(^3\)/mol respectively.

**Figure 8.** A plot of intercept versus \([\text{OH}^-]\) in os (VIII) catalysed reaction in alkaline medium. Temp. 45 C

**Figure 9.** A plot of slope versus \([\text{OH}^-]\) in os (VIII) catalysed reaction in alkaline medium. Temp. 45 C

Further evaluation of rate constants from Eq. (21) was done by making a graph \([\text{OH}^-]\) versus \(1/k\) at different but constant concentrations of alcohol that also produced linear lines crossing through origin (Figure 10). The intercept \((I_2)\) and slope \((S_2)\) evaluated from this graph are given by Eqs. (24) and (25), respectively.

\[
(I_2) = \frac{1 + K_2 [\text{CA}]}{K_1 K_2 [\text{CA}]} \tag{24}
\]

and

\[
(S_2) = \frac{K_1 + K_1 K_3 [\text{CA}]}{K_1 K_2 [\text{CA}]} \tag{25}
\]

Since the kinetic analysis of hydroxide ion concentration was limited at only one concentration of crotyl alcohol, this constrained our efforts of graphical analysis for evaluation of \(K_2\) and \(K_3\) respectively. Nevertheless, these values were calculated by rearranging Eqs. (24) and (25), respectively. Further, reemploying earlier determined values of \(k_1\) and \(K_1\) in rearranged Eqs, \(K_2\) and \(K_3\) respectively were calculated.

From Eq. (24)

\[
(I_2) k_1 = \frac{1}{K_2 [\text{CA}]} + 1
\]
Figure 10. A plot of $1/k$ versus $[\text{OH}^-]$ in os(VIII) catalysed reaction in alkaline medium.

$[\text{CAT}] = 2 \times 10^{-3}$ mol/dm$^3$; $[\text{CA}] = 5 \times 10^{-2}$ mol/dm$^3$; $[\text{Os(VIII)}] = 5 \times 10^{-5}$ mol/dm$^3$; $[I] = 1.0$ mol/dm$^3$; • 40; ■ 45 and ▲ 50 C

or

$$[(I_2)k_1-1] = \frac{1}{K_2[CA]}$$

or $K_2 = \frac{1}{(I_2)(k_1-1)[CA]}$ (26)

similarly from Eq. (25)

$$(S_2) = \frac{K_1}{k_1K_2[CA]} + \frac{K_1K_3}{k_1K_2}$$

$$= K_1 \left( I_2 \frac{1}{k_1} \right) + \frac{K_1K_3}{k_1K_2}$$ (26)

The value of ‘$K_3$’ was determined from this Eq. (26) which was found to be $17.06 \times 10^{-2}$.

The manner of transfer of electron from the alcohol to the oxidant in catalysed oxidation by Os(VIII) can be represented by scheme – 2.

A complex ion is formed between Os(VIII) species and crotyl alcohol in which hydrogen anion transfer from the $\alpha$-carbon atom of alcohol reduces the complex which on attack by a molecule of chloramine-T releases the catalyst and a process of two electrons are consummated on reduction of chloramine-T.

3. Experimental

3.1. Materials and method

Sodium salt of $N$-chloro-4-methylbenzene sulphonamide (chloramine-T) was procured (98%, E. Merck Ltd, Mumbai, Maharashtra, India) and was in practice as received. Since the salt is highly soluble in water, an aqueous solution of the reagent (~0.1 mol/dm$^{-3}$) is sufficiently stable provided it is kept in dark coloured bottles at refrigerated temperature (~5 C). The solution of chloramine-T was standardized iodometrically [33,34]. All other reagents were of analytical grade and were employed as supplied. Double distilled water was used in the study which was distilled from alkaline permanganate.
3.2. Kinetic procedure

Reaction mixtures were clutched in glass stoppered erlenmeyer flasks which were painted dark from the outside, these flasks were immersed in an isothermal water bath at ±0.1 °C. The reactions were normally initiated by adding temperature preequilibrated solution of chloramine-T and the initiation time was estimated when fifty percent of the contents from the pipette were discharged into reaction mixture. An exact fraction (5 cm³) of the reaction mixture was taken out at regular intervals and then assessed iodometrically.

Initial rates \( (k_i, \text{ mol/dm}^3\text{s}^{-1}) \) were reckoned by applying plain mirror method [35]. Pseudo I order and second order graphs were also made for comparable concentrations of the reactants and wherever reaction conditions permitted. The rates in triplicate were duplicable to within ±2%.

3.3. Stoichiometry

The reaction stoichiometry was calculated by employing surplus amount of chloramine-T over that of substrate under experimental kinetic conditions. This reaction was remained to take place in isothermal water bath more than 6 ca h after conforming of the reaction completion (test of the alcohol was negative). Excess chloramine-T was analysed iodometrically, the results show that a mole of substrate entails a mole of oxidant in the reaction as shown by Eq. (28).

\[
\text{CH}_3 - \text{CH} = \text{CH-CH}_2 - \text{OH} + \text{RNHCl} \rightarrow \text{CH}_3 - \text{CH} = \text{CH} - \text{CHO} + \text{RNH}_2 + \text{HCl}, \quad (27)
\]

where R stands for \( \text{CH}_3 \text{C}_6\text{H}_4\text{SO}_2^- \).
The reduction product of chloramine-T as p-toluene sulphonamide was later on confirmed qualitatively [26].

3.4. Product analysis

The oxidation product of crotyl alcohol was identified as crotonaldehyde and the product derivative hydrazone was confirmed with the help of chromatography, IR, NMR and mass spectroscopy. The product of crotyl alcohol also gives the silver mirror with Tollén’s reagent (ammonical silver nitrate).

The characterization of the product was made by thin layer chromatography (TLC). Thin layer chromatograms were conducted on Merck silica gel G plates in ethyl acetate: chloroform (8:2) and in the column chromatographic fractionations silica gel (60–120 mesh) used. Spots on TLC plates were visualized by spraying with 2% ceric ammonium sulphate in 2N H₂SO₄ or with iodine vapours.

Such a product was then characterized by employing various instrumental techniques such as follows:

**IR spectral analysis** The IR spectrum (Figure 11) showed absorption band at 2720–2820 cm⁻¹ C-H stretching frequency of aldehydic group due to Fermi resonance. The absorption band at 1705 cm⁻¹ indicates the presence of C=O of carbonyl group. The absorption band at 2950 cm⁻¹ indicates the C-H stretching frequency. The band at 1456 cm⁻¹ indicates the C-H asymmetric bending vibrations and at 1367 cm⁻¹ C-H symmetry bending vibration of CH₃ group.

![Figure 11. IR spectra of crotonaldehyde.](image)

**¹H NMR analysis** ¹H NMR spectrum was also obtained in CDCl₃ employing 300MHz spectrometer using TMS as reference (Figure 12). In ¹H NMR spectrum signal at 6.98 ppm is due to aldehydic group. A
doublet at δ6.05 ppm is due to =C-H proton adjacent to aldehydic group. A quintet at δ6.65 ppm is due to
=C-H proton adjacent to methyl group. A doublet at δ1.71 ppm is due to methyl group of crotonaldehyde.

**Figure 12.** $^1$H NMR spectra of crotonaldehyde.

**2, 4-dinitrophenylhydrazone derivative** Method of preparation: suspend 0.25 g of 2,4-dinitrophenylhydrazone in 5 ml of methanol and add 0.5 mL of concentrated sulphuric acid cautiously. Warm the solution. Filter the warm solution if necessary and add a solution of 2 mL crotonaldehyde in 1 mL of methanol. Filter the derivative formed and recrystallise from methanol or ethanol. Melting point 190 °C was recorded in soft glass capillaries in an electrothermal melting point apparatus.

**IR spectral analysis of 2, 4-dinitrophenylhydrazone** The important peaks observed in the infrared spectrum were at 3300 cm$^{-1}$ indicates the presence of N-H stretching frequency of a secondary amine (Figure 13). Whereas in spectrum of 2,4-dinitrophenyl hydrazine this peak is in doublet form showing N-H stretching frequency of primary amine (Figure 14). The absorption band at 1500 (N-O stretching), 1150 (N=C stretching), 1450 and 1360 cm$^{-1}$ (-CH$_2$ bending) were observed.

**$^1$H NMR analysis of 2, 4-dinitrophenylhydrazone** $^1$H NMR spectrum was obtained by dissolving hydrazone derivative of product in CDCl$_3$ using TMS as reference (Figure 15). In $^1$H NMR spectrum proton of -NH was indicated at δ6.0 ppm as a singlet. A singlet at δ6.2ppm was obtained for CH- proton adjacent to NH- group. A multiplet was obtained in the range δ7.0–9.0 ppm that attributes to the presence of aromatic protons.
Figure 13. IR spectra of 2,4-dinitrophenylhydrazone.

Figure 14. IR spectra of 2,4-dinitrophenylhydrazine.
Figure 15. $^1$H NMR spectra of 2,4-dinitrophenylhydrazone.
Mass spectral analysis of 2, 4-dinitrophenylhydrazone. Mass spectra of 2,4-dinitrophenyl hydrazone of crotonaldehyde show molecular ion peak as base peak at 250 (Figure 16).

**Figure 16.** Mass spectra of 2,4-dinitrophenylhydrazone.
4. Conclusion
In uncatalysed reaction, the order is one with respect to the alcohol and oxidant each and rate is decelerated by hydrogen cation concentration. The kinetic evidence adequately substantiates a complex between Os(VIII), crotyl alcohol. The first order dependence with respect to chloramine-T suggests a ternary activated complex comprising oxidant, substrate and catalyst anion such an activated complex being bulky in nature ensues intramolecular hydrogen anion transfer from the alcohol to the oxidant which in turn further undergoes redox decomposition. It shows that electron deficient metal centre of the catalyst being coordinated through oxygen if crotyl alcohol exposes latter to the attack by the oxidant.

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Conflict of interest
There is no conflict of interest.

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