PART - ONE

PERIODATE OXIDATIONS OF ORGANIC
SUBSTRATES IN AQUEOUS ALKALINE MEDIUM.
CHAPTER I

OXIDATION OF ALLYL ALCOHOL BY PERIODATE IN AQUEOUS ALKALINE MEDIUM.
The activity of periodate as an oxidizing agent varies greatly as a function of pH and is capable of subtle control. In acid solution, it is one of the most powerful oxidizing agents known, quantitatively and rapidly converting manganese(II) salts to permanganate, while in alkaline solution, it is slightly less oxidizing than hypochlorite. In alkaline medium, periodate is known to exist as different species involving multiple equilibria$^1$ and it needs to know its active form in the reaction.

Despite the ease with which periodates perform all the oxidations, effected by iodate, they have not been used in inorganic preparative and analytical operations; titration with NaIO$_4$ has been suggested for analyzing$^2$ mixtures of S$^{2-}$, SO$_3^{2-}$, HSO$_3^-$, S$_2$O$_4^{2-}$ and S$_2$O$_3^{2-}$.

However, there are numerous reports of the oxidation of organic compounds by periodic acid or periodates$^3$ not merely in conjunction with perchloric acid in the "wet fire" destructive oxidation of organic compounds$^4$, but as a reagent able to execute a number of well defined reactions. The specific cleavage of 1,2-diols has widely been exploited in
the realm of carbohydrates and nucleic acids, and the mechanism has been well established. In rigid systems only cis-functional groups are oxidized, the specificity being due to the cyclic intermediate. Periodate has also been applied to the oxidation of phenols (to quinones), sulphides (to sulphoxides) and hydrazine derivative:

\[ \text{IO}_4^- \rightarrow R_3\text{CNH.NH}_2 \rightarrow R_3\text{CH} + \text{N}_2 \]

Allyl alcohol finds a number of industrial applications in the preparation of resins, plasticisers, pharmaceuticals and many organic compounds. Kinetic 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 reported.

Even though periodate is a very potentive oxidant in acid medium, the oxidation of allyl alcohol by periodate did not take place even in presence of active catalysts like ruthenium, osmium etc. in acid medium. Hence, we have investigated the kinetics of oxidation of allyl alcohol by
periodate in aqueous alkaline medium. Herein we furnish the results of such study.

EXPERIMENTAL

All the chemicals used were of reagent grade and doubly distilled water was used throughout the work. The stock solution of periodate was prepared by dissolving a known weight of potassium meta periodate (Riedel) in water and was used after keeping for 24 h. The concentration of the solution was verified by titration with standard sodium thiosulphate solution iodometrically at neutral pH maintained by potassium phosphate, dibasic \((\text{K}_2\text{HPO}_4)\) and potassium phosphate, monobasic \((\text{KH}_2\text{PO}_4)\) using starch indicator.

Allyl alcohol was refluxed 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 was collected and used to prepare stock solutions of allyl alcohol. The stock solution of allyl alcohol was
standardized by the addition of excess of chloramine-T, followed by iodometric estimation of the excess.

Sodium thiosulphate (Fischer) was prepared in water. It was standardized against potassium iodate as follows: to the potassium iodide 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 indicator. Sodium perchlorate which was found to be inactive was used to maintain constant ionic strength and sodium hydroxide (AnalaR) was used to get the required alkalinity. Potassium iodate solution was prepared by dissolving a known amount of potassium iodate (Reechem) in water.

**Kinetics**

All kinetic runs were carried out under pseudo-first order conditions at 25.0 ± 0.1°C unless otherwise stated. The reaction was initiated by mixing previously thermostatted solutions of periodate and allyl alcohol, which also contained the required amounts of NaOH and NaClO$_4$ in different stoppered
bottles. The first solution contained the required concentrations of substrate, allyl alcohol, sodium hydroxide and sodium perchlorate, as a source of ionic strength and the second solution was that of oxidant, periodate, of required concentration. The reaction was followed by determining the concentration of unreacted periodate as follows: 5.0 cm$^3$ of reaction mixture was pipetted into an iodine flask containing 5.0 cm$^3$ of 10% potassium iodide solution and a calculated amount of potassium phosphate (dibasic) was added to result in neutral pH. The iodine liberated by periodate was titrated against standard sodium thiosulphate solution using starch as an indicator. Under these conditions, IO$_3^-$ was without any effect on the added I$^-$ and IO$_4^-$ was quantitatively reduced to IO$_3^-$.

Such titrations were carried out at regular intervals of time. A sample run is shown in Table I(i) (p.66).

It was found that at different initial concentrations of periodate, the plots of log [IO$_4^-$] versus time were linear to over more than two half-lives of the reaction. This showed an unit order dependence on the periodate concentration which is also supported by the
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Burette Reading (cm³)</th>
<th>$10^3[IO_4^-]$ (mol dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7.7</td>
<td>3.85</td>
</tr>
<tr>
<td>5.0</td>
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<td>380.0</td>
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</tbody>
</table>

ERROR ± 4%
constancy of rate constants at different concentrations of periodate. The duplicate runs were reproducible within ±4%. (Figure I(i) p.68).

At room temperature and in alkaline medium allyl alcohol was not hydrolyzed to any significant extent.

The effect of dissolved oxygen on the rate of the reaction was tested by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results, in presence and absence of air was obtained.

In view of the ubiquitous contamination of carbonate in basic solutions, the effect of carbonate on the reaction was studied. The carbonate up to $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ showed no effect on the reaction rate.
FIGURE I(i): FIRST ORDER PLOTS: PERIODATE OXIDATION OF ALLYL ALCOHOL IN AQUEOUS ALKALINE MEDIUM AT 25°C. (CONDITIONS AS IN TABLE III) p. 79.)
RESULTS

Stoichiometry

Different sets of reaction mixtures containing different concentrations of periodate and allyl alcohol at constant concentrations of sodium hydroxide and sodium perchlorate were allowed to react for 24 h at 25°C and then analyzed. When periodate concentration was higher than that of allyl alcohol, the total oxidant concentration was found by iodometry and after accounting for the remaining oxidant concentration, the concentration of iodate formed was derived. While, under the condition, \([\text{AA}] > [\text{IO}_4^-]\), when the periodate had fully reacted, the unreacted allyl alcohol was estimated by addition of an excess of chloramine-T followed by iodometric titration. Acrolein was found to be the main product as evidenced by spot test 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 product, iodate, was determined iodometrically in 1.0 mol dm\(^{-3}\) sulphuric acid. The results were in agreement with a 1:1
stoichiometry (equation 1) (Table I(ii) p.71)

\[ \text{CH}_2=\text{CH} \cdot \text{CH}_2\text{OH} + \text{IO}_4^- \rightarrow \text{CH}_2=\text{CH} \cdot \text{CHO} + \text{IO}_3^- + \text{H}_2\text{O} \]  

(1)

**REACTION ORDERS**

The kinetic runs of oxidation of allyl alcohol by periodate in alkaline medium were followed at different initial concentrations of oxidant, substrate and alkali in turn keeping all other concentrations constant. With increase of each of \([\text{IO}_4^-], [\text{AA}]\) and \([\text{OH}^-]\), showed the positive dependence on the rate of the reaction. The initial rates were obtained from the slopes of concentration versus time curves at the initial stages of the reaction by the plane mirror method\(^\text{13}\) and were reproducible to within ±4%.

*Effect of Periodate*

The periodate concentration was varied in the range of \(1.0 \times 10^{-4}\) to \(1.0 \times 10^{-3}\) mol dm\(^{-3}\) at constant concentration of allyl alcohol, alkali and perchlorate as in Table I(iii) (p.73). The plot of log (initial rate) versus log \([\text{IO}_4^-]\)
TABLE I(ii)

STOICHIOMETRY OF PERIODATE OXIDATION OF ALLYL ALCOHOL IN AQUEOUS ALKALINE MEDIUM AT 25 °C

\[ [\text{OH}^-] = 0.20; I = 0.60/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>(10^2[\text{IO}_4^-]^*)</th>
<th>(10^2[\text{AA}]^*)</th>
<th>(10^2[\text{IO}_4^-]^*)</th>
<th>(10^2[\text{AA}]^*)</th>
<th>(10^2[\text{IO}_3^-]^*)</th>
</tr>
</thead>
<tbody>
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<td>0.56</td>
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<td>0.47</td>
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</table>

ERROR ± 4%

* ALL CONCENTRATIONS ARE IN \(\text{mol dm}^{-3}\).
showed the order of reaction in periodate concentration as unity (Figure I(ii) p.74).

**Effect of Allyl alcohol**

From the plot of log (initial rate) versus log [AA], the order of reaction in [AA] was found to be less than unity in the concentration range of $2.0 \times 10^{-2}$ to $2.0 \times 10^{-1}$ mol dm$^{-3}$ (Table I(iii) p.73) (Figure I(ii) p.74).

**Effect of Alkali**

The alkali concentration was varied in the range of $5.0 \times 10^{-2}$ to $5.0 \times 10^{-1}$ mol dm$^{-3}$ keeping all other conditions constant as shown in Table I(iii) (p.73). The order with respect to alkali was less than unity (Figure I(ii) p.74).
<table>
<thead>
<tr>
<th>$10^2[AA]$</th>
<th>$10^3[IO_4^-]$</th>
<th>$10[OH^-]$</th>
<th>$10^6$(Int.Rate)</th>
<th>$10^5k_u$</th>
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<td>mol dm$^{-3}$</td>
<td>mol dm$^{-3}$ s$^{-1}$</td>
<td>s$^{-1}$</td>
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</table>

**ERROR ± 4%**

*Calculation of rate constants was on the basis of rate law (18) and $K_1 = 3.20$ dm$^3$ mol$^{-1}$, $K_2 = 4.42$ dm$^3$ mol$^{-1}$ AND $k = 1.0 \times 10^{-3}$ s$^{-1}$.*
FIGURE III: ORDER IN $[\text{IO}_4^-]$, $[\text{AA}]$ AND $[\text{OH}^-]$: PERIODATE OXIDATION OF ALLYL ALCOHOL IN AQUEOUS ALKALINE MEDIUM AT 25°C; (CONDITIONS AS IN TABLE III (p. 73)).
Effect of added products

The effect of initially added products, iodate and acrolein each in the concentration range of $1.0 \times 10^{-3}$ to $8.0 \times 10^{-3}$ mol dm$^{-3}$, all other conditions being constant did not affect the title reaction (Table I(iv) p.76).

Effect of dielectric constant (D)

The dielectric constant of the reaction medium was varied by using t-butanol (Baker) content (V/V) in the reaction mixture. Earlier, the inertness of the t-butanol towards oxidant in the reaction mixture had been confirmed. Since dielectric constants for various percentages of t-butanol (V/V) are not available in literature, they were computed from the values of pure liquids$^{14}$ using equation (2) as in earlier work$^{15}$.

$$D = D_1 V_1 + D_2 V_2$$

(2)

where $V_1$ and $V_2$ are volume fractions and $D_1$ and $D_2$ are dielectric constants of water and t-butanol respectively.

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TABLE I

EFFECT OF INITIAL ADDITION OF PRODUCTS, IO₃⁻ AND ACROLEIN ON PERIODATE OXIDATION OF ALLYL ALCOHOL IN AQUEOUS ALKALINE MEDIUM AT 25°C.

[IO₄⁻]=4.0×10⁻³; [AA]=4.0×10⁻²; [OH⁻]=0.20; I=0.60/mol dm⁻³.

<table>
<thead>
<tr>
<th>10^3[Acrolein]</th>
<th>10^3[IO₃⁻]</th>
<th>10^5kₜᵤ</th>
</tr>
</thead>
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</table>
Under the constant concentrations at \([{\text{IO}_4}^-] = 4.0 \times 10^{-3}; [{\text{AA}}] = 4.0 \times 10^{-2}; [{\text{OH}}^-] = 0.20\) and \(I = 0.60\) \(\text{mol dm}^{-3}\), with the increase of t-butanol content in the reaction mixture from 0.0 to 40.0 \%(V/V), the rate remained almost unchanged (Table I(v) p.78).

**Effect of ionic strength**

The ionic strength of the reaction medium was varied from \(6.0 \times 10^{-2}\) to \(6.0 \times 10^{-1}\) \(\text{mol dm}^{-3}\) using sodium perchlorate which was found to be inert and the kinetic study was carried out at constant conditions as shown in Table I(v) (p.78). No appreciable change in the reaction rate was observed indicating the negligible effect of ionic strength on the reaction rate.

**Test for free radicals**

The intervention of free radicals in the reaction was examined as follows: the reaction mixture to which a known quantity of acrylamide had been added initially, was kept for 24 h in an inert atmosphere. On diluting the reaction mixture
TABLE I:

EFFECT OF DIELECTRIC CONSTANT (D) AND IONIC STRENGTH ON PERIODATE OXIDATION OF ALLYL ALCOHOL IN AQUEOUS ALKALINE MEDIUM AT 25°C. I = 0.6 mol dm$^{-3}$

$[\text{IO}_4^-]=4.0 \times 10^{-3}; [\text{AA}]=4.0 \times 10^{-2}; [\text{OH}^-]=0.20$/mol dm$^{-3}$

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

<table>
<thead>
<tr>
<th>% t-butanol</th>
<th>D V/V</th>
<th>$10^5k_U$ s$^{-1}$</th>
<th>I mol dm$^{-3}$</th>
<th>$10^5k_U$ s$^{-1}$</th>
</tr>
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<td>0.60</td>
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</table>
with methanol a copious precipitate resulted suggesting the possibility of free radical intervention in the reaction.

**Effect of temperature**

The activation parameters for the reaction were studied by using linear regression analysis (also known as the method of least squares)\(^{16}\). In generalized notation, the formula for a straight line is

\[
y = ax + b
\]

The most tractable form of linear regression analysis assumes that values of the independent variable \(x\) are known without error and that experimental error is manifested only in values of the dependent variable \(y\). Most sets of kinetic data approximate this situation, in as much as the times of observation are more accurately measurable than the chemical or physical quantities related to reactant concentrations. The straight line selected by common linear regression analysis is that which minimizes the sum of squares of the deviations of the \(y\) variable from the line.
The slope, 'a', and intercept, 'b', parameters for the above equation can be calculated by linear regression analysis by any of several mathematically equivalent but different-looking expressions. Most familiar are

\[
\text{Slope: } a = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}
\]

\[
\text{Intercept: } b = \frac{\sum y \sum x^2 - \sum x \sum xy}{n \sum x^2 - (\sum x)^2}
\]

where n is the number of data points and the summations are for all data points in the set.

To evaluate the activation parameters, the oxidation of allyl alcohol by periodate was studied at four different temperatures, at constant ionic strength and constant alkalinity. The rate constants (k) of the slow step of scheme 1 were obtained from the intercepts of 1/k versus 1/[AA] plots at 25, 30, 35 and 40°C and the values of k (s\(^{-1}\)) were obtained as \(1.0 \times 10^{-3}\), \(1.55 \times 10^{-3}\), \(2.27 \times 10^{-3}\) and \(3.31 \times 10^{-3}\) respectively. Least square analysis of the data gave the graph of \(\log k_2\) versus 1/T and hence, activation energy of the reaction
The entropy and energy of activation were calculated from

\[
E_a = -2.303 \times R \times \text{slope}
\]

\[
\frac{\Delta S^\#}{4.576} = \log k - 10.753 - \log T + \frac{E_a}{4.576 T}
\]

The results are given in Table I(vi) (p.82).

**DISCUSSION**

The activity of periodate as an oxidizing agent varies greatly as a function of pH and is capable of subtle control. In acid solution, it is one of the most powerful oxidizing agents known, while in alkaline solution, it is slightly less so. However, in an aqueous alkaline medium and in the pH range employed in the present study, periodate cannot exist as H\(_4\)IO\(_6\)\(^-\). Because, in aqueous solution, periodate is involved in equilibria (3) to (5) depending on the pH of the solution.
TABLE I(vi)

EFFECT OF TEMPERATURE ON PERIODATE OXIDATION OF ALYL ALCOHOL IN AQUEOUS ALKALINE MEDIUM; I = 0.6 mol dm$^{-3}$

$[IO_4^{-}]=4.0 \times 10^{-3}$; $[AA]=4.0 \times 10^{-2}$; $[OH^{-}]=0.20; I=0.60$/mol dm$^{-3}$

<table>
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<tr>
<th>$10^31/T$ (x)</th>
<th>$\log k_2$ (y)</th>
<th>$10^3$ (xy)</th>
<th>$10^6$ ($x^2$)</th>
<th>$y_{cal}$</th>
</tr>
</thead>
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</table>

$\Sigma x=6.552$  $\Sigma xy=-19.038$  $\Sigma x^2=21.466$

| 3.143         | -2.480        | -7.795      | 9.878          | -2.482   |

$\Sigma x=6.336$  $\Sigma xy=-16.237$  $\Sigma x^2=20.073$

$E_a = 60.0 \pm 2.0$ k J mol$^{-1}$

$\Delta S^\# = -110.0 \pm 3.0$ J K$^{-1}$ mol$^{-1}$

ERROR $\pm$ 4%
FIGURE I(IV): EFFECT OF TEMPERATURE: PERIODATE OXIDATION OF ALLYL ALCOHOL IN AQUEOUS ALKALINE MEDIUM; (CONDITIONS AS IN TABLE II(v) p. 82).
The species $H\textsubscript{2}IO\textsuperscript{-}$ exists near pH 7.0. Hence, under the alkaline conditions employed in the present system, the main species would be expected to be trihydrogen para periodate, $H\textsubscript{3}IO\textsuperscript{2-}$ and dihydrogen para periodate, $H\textsubscript{2}IO\textsuperscript{3-}$. At higher concentrations, periodate can also undergo dimerization. The observed fractional order in [alkali] may be understood in terms of $H\textsubscript{2}IO\textsuperscript{3-}$ as the main species in alkaline medium with the following equilibrium (6):

$$H\textsubscript{3}IO\textsuperscript{2-} + OH^- \rightleftharpoons K \quad H\textsubscript{2}IO\textsuperscript{3-} + H\textsubscript{2}O$$

The fractional order in substrate concentration, [AA], and intercept of the plot of $1/k$ versus $1/[AA]$ (Figure I(iv) p.92) indicates that the reaction occurs through formation of a complex between alkaline species of oxidant and substrate followed by its decomposition to yield products in
the subsequent fast step (Scheme). Such type of oxidant-substrate complex may be expected because of the order in allyl alcohol is less than unity. Attempts to obtain spectral evidence for such a complex were in vain, since no appreciable change resulting in the spectrum of the substrate or oxidant in presence of each other. A feeble interaction is probably involved. However, the plot of 1/k versus 1/[AA] was fairly linear with a non-zero intercept supporting the formation of a complex between the oxidant and substrate. Such oxidant-substrate complexes are reported in earlier works also. 12,16

Thus, the following scheme may be proposed in accordance with the observed rate law including free radical intervention.
Scheme leads to the rate law (10)

\[
\text{Rate} = \frac{d[\text{IO}^4^-]}{dt} = \frac{k_1 K_1 K_2 [\text{H}_2\text{IO}_6^{2-}]_T [\text{CH}_2=\text{CH} \cdot \text{CHOH}]_T [\text{CH}^-]_T}{1 + k_1 [\text{OH}^-] + k_1 K_2 [\text{AA}] [\text{OH}^-]}
\]  

(10)

It can be derived as follows:

From equation (8), the rate of disappearance of periodate is given by
Rate = \frac{d[\text{IO}_4^-]}{dt} = k [C] \quad (11)

The concentration of complex results from equation (7) as,

\[ [C] = K [\text{CH}_2=\text{CH}.\text{CH}_2\text{OH}] [\text{H}_2\text{IO}_6^{3-}] \quad (12) \]

From step (6),

\[ K_1 = \frac{[\text{H}_2\text{IO}_6^{3-}]}{[\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-]} \quad (13) \]

Substituting the value for [C] using equations (12) and (13), equation (11) assumes the form,

\[ \frac{d[\text{IO}_4^-]}{dt} = k K_2 [\text{CH}_2=\text{CH}.\text{CH}_2\text{OH}] [\text{H}_2\text{IO}_6^{3-}] \]

\[ = k K_1 K_2 [\text{CH}_2=\text{CH}.\text{CH}_2\text{OH}] [\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-] \quad (14) \]

The total concentration of periodate, \([\text{H}_3\text{IO}_6^{2-}]_T\), in terms of three periodate species that might be present in solution, may be expressed as,
\[
[H_3IO_6^{2-}]_T = [H_3IO_6^{2-}]_f + [H_2IO_6^{3-}] + [C]
\]
\[
= [H_3IO_6^{2-}]_f + K_1 [H_3IO_6^{2-}]_f [OH^-]
\]
\[
= [H_3IO_6^{2-}]_f + K_1 [H_3IO_6^{2-}]_f [OH^-]
\]
\[+ K_1 K_2 [CH_2=CH.CH_2OH] [H_3IO_6^{2-}]_f [OH^-] \]
\[
= [H_3IO_6^{2-}]_f \left\{1 + K_1 [OH^-] + K_1 K_2 [CH_2=CH.CH_2OH] [OH^-] \right\}
\]
\[
\therefore [H_3IO_6^{2-}]_f = \frac{[H_3IO_6^{2-}]_T}{1 + K_1 [OH^-] + K_1 K_2 [CH_2=CH.CH_2OH] [OH^-]} \quad (15)
\]

The total concentration of the substrate,
\[[CH_2=CH.CH_2OH]_T, is given by,
\[
[CH_2=CH.CH_2OH]_T = [CH_2=CH.CH_2OH]_f + [C]
\]
\[
= [CH_2=CH.CH_2OH]_f + K_2 [CH_2=CH.CH_2OH]_f [H_2IO_6^{3-}]
\]
\[
= [CH_2=CH.CH_2OH]_f \left\{1 + K_2 [H_2IO_6^{3-}] \right\}
\]
\[
\begin{align*}
\therefore [\text{CH}_2=\text{CH} \cdot \text{CH}_2\text{OH}]_f &= \frac{[\text{CH}_2=\text{CH} \cdot \text{CH}_2\text{OH}]_T}{1 + K_2 [\text{H}_2\text{IO}_6^{3-}]} \\
\end{align*}
\]

Since \(K_2[\text{H}_2\text{IO}_6^{3-}]\) is too small compared to unity,

\[
[\text{CH}_2=\text{CH} \cdot \text{CH}_2\text{OH}]_T = [\text{CH}_2=\text{CH} \cdot \text{CH}_2\text{OH}]_f \tag{16}
\]

Similarly, total alkali concentration, \([\text{OH}^-]_T\), may be obtained as,

\[
[\text{OH}^-]_T = [\text{OH}^-]_f + [\text{H}_2\text{IO}_6^{3-}]
\]

\[
= [\text{OH}^-]_f + K_1 [\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-]_f
\]

or,

\[
[\text{OH}^-]_f = \frac{[\text{OH}^-]_T}{1 + K_1 [\text{H}_3\text{IO}_6^{2-}]} \approx [\text{OH}^-]_T \tag{17}
\]

By substituting the values of \([\text{H}_3\text{IO}_6^{2-}]_f\), \([\text{CH}_2=\text{CH} \cdot \text{CH}_2\text{OH}]_f\) and \([\text{OH}^-]_f\) from equations (15), (16) and (17) in equation (14) rate law (18) is obtained.

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Rate law:

\[
\text{Rate} = \frac{d[IO_4^-]}{dt} = \frac{k_1 K_1 K_2 [AA] [IO_4^-] [OH^-]_T}{1 + K_1 [OH^-] + K_1 K_2 [AA] [OH^-]_T}
\]  

(18)

in which \([H_3IO_2^-]_f\) and \([CH_2=CH_2OH]_f\) are written as \([IO_4^-]_f\) and \([AA]_f\) respectively.

Verification of the derived rate law

The rate equation (18) may be rearranged as equation (19) which is suitable for verification.

\[
\frac{[IO_4^-]_T}{\text{rate}} = \frac{1}{k} = \frac{1}{k_1 K_1 K_2 [OH^-] [AA]} + \frac{1}{k_1 K_2 [AA]} + \frac{1}{k_1}
\]  

(19)

From equation (19), it is evident that the plot of left hand side versus \(1/[OH^-]\) should be linear, where all other concentrations, except \([OH^-]\), are maintained constant. Likewise, when only allyl alcohol concentration was varied, maintaining all other conditions constant, a plot of \(1/k\) versus \(1/[AA]\) is also expected to be linear. This was found to be so as seen in Figure I(iv) (p.92). From the slopes and intercepts of the plots, the values of constants, \(K_1\), \(K_2\) and \(k_1\) were evaluated as \(3.26\pm0.05 \text{ dm}^3\text{ mol}^{-1}\), \(4.42\pm0.1 \text{ dm}^3\text{ mol}^{-1}\) respectively.
and $1.0 \times 10^{-3} \pm 3.0 \times 10^{-5}$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. By using these values, the rate constants under different conditions of experiments are calculated which are in good agreement with the experimental rate constants (Table I(iii) p.73).

The negligibly small effects of ionic strength and dielectric constant on the reaction rates are presumably due to the fact that the reaction is between a neutral and a charged species which is evident from the mechanism of scheme. The sizable negative entropy of activation is in agreement with the formation of activated complex involved in the reaction.
Verifying the rate law for the periodate oxidation of allyl alcohol in aqueous alkaline medium at 25°C (conditions as in Table I(iii) p. 79).
FINDINGS

The periodate oxidation of allyl alcohol in aqueous alkaline medium has a 1:1 stoichiometry under two different extreme conditions viz. \([\text{IO}_4^-] > [\text{AA}]\) and \([\text{IO}_4^-] < [\text{AA}]\). When \([\text{AA}] > [\text{IO}_4^-]\) the reaction is of unit order in [oxidant], fractional order each in [substrate] and [alkali]. The reaction takes place via the formation of an oxidant-substrate complex and its subsequent decomposition to yield a free radical and an intermediate, \(\text{I(VI)}\), followed by the other fast step to give the products. \(\text{H}_2\text{IO}_6^{3-}\) is the active species of the oxidant.

IMPORTANCE OF RESULTS OF CHAPTER I

It is interesting to note that periodate existing as periodic acid in acid medium, being one of the strongest oxidizing agents in acid medium, oxidation of allyl alcohol in acid medium does not take place even in presence of different catalysts. But, in alkaline medium the reaction takes place with measurable velocity, thus receiving the attention to study the activity of periodate in such media.
REFERENCES


