Orientation on Electron-Transfer Nature for Oxidation of Some Water-Soluble Carbohydrates: Kinetics and Mechanism of Hexachloroiridate (IV) Oxidation of Methyl Cellulose in Aqueous Perchlorate Solutions

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Abstract The kinetics and mechanism of oxidation of methyl cellulose (MC) polysaccharide by hexachloroiridate (IV) in aqueous perchlorate solutions at a constant ionic strength of 0.1 mole dm⁻³ has been investigated, spectrophotometrically. The experimental results showed first-order dependence in [IrCl₆]²⁻ and fractional first-order kinetics with respect to the MC concentration. The reaction rate was found to increase with decreasing the [H⁺]. A kinetic evidence for formation of 1:1 intermediate complex was revealed. The reaction kinetics seems to be of considerable complexity where one chloride ion from hexachloroiridate (IV) oxidant may act as a bridging ligand between the oxidant and the substrate within the formed intermediate complex. However the added chloride ions and oxidation products were found to have negligible effects on the reaction rate, the added acrylonitrile indicated the intervention of free-radical mechanism during the oxidation process. The kinetic parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results is discussed.

Keywords: Carbohydrates, Methyl Cellulose, Hexachloroiridate(IV), Oxidation, Kinetics.

1. Introduction

Methyl cellulose (MC) is a cellulose ether derivative that is water-soluble due to the methylation of hydroxyl moieties which prevent extensive hydrogen bonding. It is hydrophilic macromolecule unless the temperature exceeds that of the lower critical temperature of solution (LCST) of the approximate range 40-70°C [1]. Therefore, this material is expected to have
advantageous for enzyme immobilization and, hence, methyl cellulose is an important macromolecule which used for preparing the nanofibrous mat through selecting the proper electro-spinning conditions [2].

The kinetics of oxidation of methyl cellulose (MC) polysaccharide by permanganate ion as multi-equivalent oxidant in alkaline solutions [3-5], showed that the oxidation reaction was proceeding through two distinct stages without free-radical intervention. On the other hand, oxidation of this MC substrate by alkaline hexacyanoferrate (III) ion as one-equivalent oxidant [6] indicated the intervention of free-radical mechanism through a simple one-step reaction-path. Kinetic evidences for formation of 1:1 intermediate complexes through those two catalyzation oxidation in either acid or base media were revealed.

Although, hexachloroiridate(IV) is known as inert oxidant of one-equivalent nature and has been widely used for oxidation of most organic and inorganic substrates, it seems that no attention has been paid to the oxidation of MC macromolecule by this oxidant.

Preliminary experiments on the oxidation of MC by [IrCl₆]³⁻ indicated that the oxidation reaction kinetics is complex whereas the influence of added acid showed an acid-inhibition of the rate constants.

In view of the above discrepancies and our interest on the kinetics of oxidation of some macromolecules by various oxidants in acidic media [5,7-14] along with the oxidation of some organic and inorganic substrate by this oxidant [15-18], the present work seems to merit an investigation with the aims at shedding more highlights on the kinetics and mechanistics of oxidation of macromolecules in terms of electron-transfer process as well as to examine the influence of oxidant nature and solvent type on the oxidation kinetics. The results obtained may gain us some univocal information on the chemistry of MC carbohydrate in aqueous acidic media with synthesize of novel keto-biodegradable polymeric precursor derivatives as chelating agents.

2. Experimental

2.1. Materials

Sodium hexachloroiridate (IV) of Analar quality (Wako Chemical Reagent) was used without further purification. The preparation and standardization of the stock solutions of [IrCl₆]³⁻ were the same as described elsewhere [14-20].

Methyl cellulose (MC) used in this work is (MP Biomedicals, LLC, France) and was used without further purification. An average molecular weight was about 86000 Dalton which calculated from the viscosity measurements of 2 % solution at 20 °C (the intrinsic viscosity was 750 ml/g and the apparent viscosity was 4000 mPas). The average degree of polymerization (DP) was 460. A stock solution was prepared as described earlier [3-5]. This process takes place by stepwise addition of the reagent powder to deionized water whilst vigorously stirring the solution to prevent the formation of coagulate lumps, which swell with difficulty.

All other reagents were of analytical grades. Doubly distilled conductivity water was used in all preparations. The temperature was controlled within ± 0.05 °C.

The ionic strength of the reaction mixtures was maintained constants at 0.1 mol dm⁻³ using NaClO₄ as a non-complexing agent.

2.2. Kinetic Measurements

A large excess of MC over that of [IrCl₆]³⁻ was employed in order to maintain the pseudo-first-order conditions throughout the kinetic measurements. The procedure of measurements was the same as described elsewhere [3-5,16-20]. The zero time was taken when half of [IrCl₆]³⁻ solution had been added to MC solution into the reaction cell. The progress of the reaction was followed by measuring the decrease in absorbance of [IrCl₆]³⁻ at its absorption maximum, 489 nm, where all other reagents of the reaction mixture do not absorb significantly at this wavelength, as a function of time. The applicability of beer’s law for [IrCl₆]³⁻ at 489 nm has been verified giving ε = 4050 ± 20 dm³ mol⁻¹ cm⁻¹ in good agreement with the values reported elsewhere [16-21]. The absorbance measurements were made in a thermostated cell compartment at the desired temperature within ± 0.05°C on a Shimadzu UV-2101/3101 PC automatic scanning double beam
spectrophotometer fitted with a wavelength program controller using cells of pathlength 1.0 cm. The spectral changes during the progress of the oxidation reaction are shown in Figure 1.

3. Results

3.1. Stoichiometry and Products Analyses

Since the kinetics of this redox reaction seems to be of complexity nature, determination of the reaction stoichiometry becomes of great importance. Reaction mixtures containing different concentrations of the reactants at \([\text{H}^+] = 1 \times 10^{-4}\) and \(I = 0.1 \text{ mol dm}^{-3}\) were equilibrated in dark bottles away from light. The unreacted \([\text{IrCl}_6]^{2-}\) was estimated periodically until it reaches a constant value. The experimental results revealed that 1.0 mole of MC consumed 4.0 ± 0.1 mol of the oxidant. This result conforms to the following stoichiometric equation.

\[
(C_7H_{12}O_5)_n + 4 [\text{IrCl}_6]^{2-} = (C_7H_8O_5)_n + 4 [\text{IrCl}_6]^{3-} + 4\text{H}^+ \tag{1}
\]

where \(C_7H_{12}O_5\) and \(C_7H_8O_5\) denote MC and its corresponding diketo-derivative, respectively. The oxidation product was identified by the spectral data and elemental analysis as described elsewhere [22-24]. The keto-derivatives were characterized by the formation of 2,4-dinitrophenylhydrazone and dioxime derivatives as well as by the IR absorption bands at 1760-1730 cm\(^{-1}\) that characterized to the carbonyl group of \(\alpha\)-diketones [25,26]. The enhancement of the absorption band of OH group in the IR spectra of the product indicated the oxidation of OH groups of methyl cellulose to its corresponding ketones.

The formed biopolymer precursor oxidation product could be used as biocatalyst in immobilization systems as well as to encapsulate, protect and deliver bioactive or functional components such as minerals, peptides, proteins, enzymes, drugs, lipids and dietary fibers.

![Figure 1](image-url)  
**Figure 1.** Spectral changes (200 - 700 nm) during the formation of intermediate complexes in the oxidation of methyl cellulose by hexachloroiridate (IV) in aqueous solutions. \([\text{IrCl}_6]^{3-} = 2\times10^{-4}, [\text{MC}] = 0.2, [\text{H}^+] = 0.6\times10^{-4}\) and \(I = 0.1 \text{ mol dm}^{-3}\) at 40 °C (scanning time intervals = 4 min).

3.2. Dependence of the Reaction Rates on \([\text{IrCl}_6]^{2-}\) and [MC]

Plots of ln (absorbance) vs. time were found to be linear for more than two-half-lives of reaction completion. This result indicated that the reaction is first-order in \([\text{IrCl}_6]^{2-}\). The first-order dependency was confirmed not only by the observed linearity of pseudo-first-order plots but also by the independence of the obtained rate constant on different initial concentrations of the oxidant used ranging between \(1\times10^{-4}\) and \(6\times10^{-4} \text{ mol dm}^{-3}\). Again some experiments were performed.
in the presence of iridium (III) as an oxidation product. The result indicates that [IrCl₆]³⁻ does not inhibit the reaction rate and, hence, the reversible reaction between MC and iridium (IV) is unlikely. The values of the pseudo first-order rate constants, \( k_{\text{obs}} \), can be evaluated from the gradients of ln (absorbance)-time plots. These values were calculated by the method of least-squares and are summarized in Table 1.

The order with respect to MC was deduced from the measurements of the reaction rates at several initial concentrations of MC and fixed concentrations of all other reagents. The non-constancy of the second-order rate constants derived from dividing the observed pseudo first-order rate constants by the initial \([MC]_0\) shown in Table 1 indicates that the rate is fractional-first order in [MC]. The magnitude of the order was calculated from the double logarithm of the observed rate constants and the concentrations of MC (\(k_{\text{obs}} = [MC]^n\)). Again, when the reciprocals of the observed rate constants were plotted against the reciprocals of the substrate, \(1/k_{\text{obs}} \) vs. \(1/[MC]\), straight lines with distinct positive intercepts on \(1/k_{\text{obs}}\) axis were observed. This behavior was found to be indicative to the Michaelis-Menten kinetics for formation of 1:1 intermediate complexes. A typical plot is shown in Figure 2.

**Table 1.** The values of the observed first-order rate constants in the oxidation of methyl cellulose by hexachloroiridate (IV) in aqueous solutions. \([IrCl_6]^{2-} = 2 \times 10^{-4}, [MC] = 0.2, I = 0.1 \text{ mol dm}^{-3}\) at 40 °C.

| \(10^4 [H^+]^a\) | \(10^4 k_{\text{obs}} \text{s}^{-1}\) | \([S]^b\) | \(10^4 k_{\text{obs}} \text{s}^{-1}\) |
|-----------------|-----------------|--------|------------------|
| 0.6             | 1.63            | 0.1    | 1.23             |
| 1.4             | 0.74            | 0.2    | 1.63             |

\(a\)- \([S]\) 0.2 mol dm\(^{-3}\); \(b\)- \([H^+]\) = 0.6 \times 10^-4 mol dm\(^{-3}\)

**Figure 2.** A reciprocal Michaelis-Menten plot in the oxidation of methyl cellulose by hexachloroiridate (IV) in aqueous solutions. \([IrCl_6]^{2-} = 2 \times 10^{-4}, [MC] = 0.2, I = 0.1 \text{ mol dm}^{-3}\) at 40 °C.

### 3.3. Dependence of the Reaction Rates on \([H^+]\)

The effect of \([H^+]\) on the rate constants at constant ionic strength of 2 \( \times 10^{-4} \) mol dm\(^{-3}\) and constants of all other reagents concentration was studied to elucidate a suitable reaction mechanism. An increase in \([H^+]\) was found to inhibit the oxidation rates. Plots of \(k_{\text{obs}}\) vs. \([H^+]\) gave curved lines passing through the origin as shown in Figure 3. On the other hand, plots of \(1/k_{\text{obs}}\) vs. \([H^+]\) found to be linear with positive intercept on \(1/k_{\text{obs}}\) axis as shown in Figure 4. A reverse fractional-first order in \([H^+]\) was revealed from \((\log k_{\text{obs}} - \log [H^+])^1\) plots.

### 3.4. Dependence of the Reaction Rates on Ionic Strength

The influence of the ionic strength on the reaction rate at constant \([H^+]\) as NaClO₄ concentration increased up to 0.6 moldm\(^{-3}\) has been examined. The results obtained indicated that the effect of the ionic strength on the reaction rates was
negligible under our experimental conditions. The observed pseudo-first-order constants at [MC] = 0.2, [IrCl₆]²⁻ =2x10⁻⁴, [H⁺] = 0.6x10⁻⁴ moldm⁻³ and 40 °C were found to be 1.60, 1.58,1.62 and 1.59x10⁻⁴ s⁻¹ at ionic strengths of 0.1, 0.2, 0.4 and 0.6 moldm⁻³, respectively.

3.5. Polymerization Test

The possibility of formation of free-radicals was examined by adding 10 % (v/v) acrylonitrile to the partially oxidized reaction mixture. After a lapse of 15 min mixing (on warming), a copious precipitate was observed indicating the intervention of the free-radical mechanism in the oxidation reaction.

3.6. Dependence of the Reaction Rates on [KCl] and [IrCl₆]³⁻

In order to investigate either the aquation of [Ir(Cl₅) H₂O] or [IrCl₆]³⁻ is the reactive species of the oxidant in the rate-determining step. Therefore, different concentrations of KCl were added to the reaction mixtures. Again, in order to examining the reaction reversibility, amount of the product [IrCl₆]³⁻ were added to the reaction mixture. It was found that the additions of either those two reagents to the reaction mixtures have no influence on the reaction rates.

![Graph 1](https://via.placeholder.com/150)

**Figure 3.** Plots of kₜₚₒₛ vs [H⁺]⁻¹ in the oxidation of methyl cellulose by hexachloroiridate (IV) in aqueous solutions. [IrCl₆]³⁻ = 2x10⁻⁴, [MC] = 0.2, [I] = 0.1 mol dm⁻³ at various temperatures and hydrogen ion concentrations.

![Graph 2](https://via.placeholder.com/150)
Figure 4. Plots of $1/k_{obs}$ vs. $[H^+]$ in the oxidation of methyl cellulose by hexachloroiridate (IV) in aqueous solutions. $[\text{IrCl}_6]^{2-} = 2\times10^{-4}$, $[\text{MC}] = 0.2$, $I = 0.1$ mol dm$^{-3}$ at various temperatures and hydrogen ion concentrations.

4. Discussion

A variety of reaction mechanisms was recognized in redox reactions involving hexachloroiridate (IV) as of one-equivalent nature [27-31]. Some of these reactions tend to proceed through formation of intermediate complexes of inner-sphere nature [14,15,21], outer-sphere type [32] or by both inner- and outer-sphere [33] mechanisms via free-radicals intervention. Other reactions are proceeding through outer-sphere mechanisms of non-free-radicals intervention [34-42], whereas the formation binuclear complexes [16,17] and ion-pairs [20] have been postulated for some other redox systems.

Polysaccharides which containing primary (R-CH$_2$-OH)$_n$, secondary (R-CH-OH)$_n$ (where R- is the macromolecule monomer) or those both alcoholic functional groups in their macromolecular chains are well-known to have high tendency for protonation in acidic solutions to form more reactive alkoxinium ions (R-CHOH$_3^+$) [5,7-10], whereas in alkali they form the reactive alkoxides (R-CH-O$^-$) by deprotonation [3,4,9-11,13].

The decrease of the rate constants with increasing the hydrogen ion concentration was surprising. Hence, this behavior can be explained by a release of protons by hydrolysis or ionization processes prior to the rate-determining steps. Since, hexachloroiridate (IV) is known to be extremely inert [21], the release of proton from the oxidant is excluded. Again under our experimental conditions of lower [H$^+$], the protonation of MC seems to be difficult or negligible small and, hence, it is also excluded. Consequently, the observed inverse fractional-order in [H$^+$] in the present oxidation reaction may indicate the existence of a reaction-path involving a release of one proton prior to the rate-determining step.

In view of the aforementioned arguments and under the experimental conditions used of lower acid concentrations, a mechanism in consistent with the observed kinetic results which may be suggested involves the attack of the oxidant to the center of the substrate forming an intermediate complex (C$_1$) with releasing a proton,

$$\text{Ox} + S \xrightarrow{K_1} C_1 + \text{H}_2\text{O}^+$$

(2)

followed by decomposition of the formed complex (C$_1$) in the rate-determining step to give rise to a substrate free-radical and hexachloroiridate (III) as initial oxidation products,

$$C_1 \xrightarrow{K} C_1^- + \text{Red}$$

(3)

$$C_1^- + \text{Ox} \xrightarrow{\text{fast}} \text{final oxidation products}$$

(4)

where $K_1$ is the formation constant of the complex, the symbol (Ox) represents to the $[\text{IrCl}_6]^{2-}$, (Red) denotes the $[\text{IrCl}_6]^3-$ and $S$ is the substrate, respectively. This suggestion is supported by the released protons in the stoichiometric reaction defined by Eq. (1), as well as obeying the oxidation reaction to the Michaelis-Menten kinetics (Figure 2). The change of the rate constants with the change in the hydrogen ion and substrate concentrations can be expressed by the following rate-law equation

$$\text{Rate} = \frac{-d[\text{Ox}]}{dt} = \frac{kK_1[S][H^+]^{-1}[\text{Ox}]_T}{1 + K_1[S][H^+]^{-1}}$$

(5)

where $[\text{Ox}]_T$ is the total analytical concentration of oxidant. Under pseudo first-order conditions of the presence of a large excess of substrate [S] over that of the [Ox], Eq. (5) can be rewritten in the following form

$$\frac{1}{k_{obs}} = \frac{[H^+]}{kK_1[S]} + \frac{1}{k}$$

(6)

The rate law expression (6) requires that either $1/k_{obs}$-$1/[S]$ at constant [H$^+$] or $1/k_{obs}$-$1/[H^+]$ at constant [S] plots to be linear with positive intercept on $1/k_{obs}$ axes. The experimental results were found to satisfy this requirement. However, this relationship did not agree with the kinetic results since the magnitudes of the intercepts obtained from those two plots...
(which are corresponding to the elementary rate constant (k)) were found to be quite different at the same temperature. Therefore, an alternative mechanism could be suggested. It involves the formation of an intermediate complex (C₁) at first. Then, some rearrangement of that complex was occurred with releasing a hydronium ion to give the more reactive complex (C₂) as follows,

\[
\text{Ox} + S \xrightleftharpoons[k_1]{K} C_1 \xrightleftharpoons[k_2]{K} C_2 + \text{H}_3\text{O}^+ \tag{7}
\]

\[
C_2 \xrightarrow{K} \text{C}_2 + \text{Red} \ (\text{initial oxidation products}) \tag{8}
\]

In a similar manner of the derivation of the above mechanism the following rate-law expression is obtained,

\[
\frac{1}{k_{\text{obs}}} = \frac{[\text{H}^+]}{kK_1K_2[S]} + \frac{[\text{H}^+]}{kK_2} + \frac{1}{k} \tag{9}
\]

According to Eq. (9) plots of either 1/k_{obs} vs. 1/[S] at constant [H⁺] or 1/k_{obs} vs. 1/[H⁺] at constant [S], respectively, gave straight lines with positive intercepts on 1/k_{obs} axes, from whose slopes and intercepts the values of the various rate constants can be evaluated.

The values of the rate constants of the elementary reaction (k) and the apparent rate constants (kK₁K₂) at different temperatures were calculated from the temperature dependence of the rate constants at various [H⁺] and fixed substrate concentration using the least-squares method and are summarized in Table 2. Again, the formation constant (K₁) was evaluated from the slopes and intercepts of those two plots and found to be 8.13± 0.5 dm³ mol⁻¹ at 40 °C.

The negative value of ΔS° may confirm the compactness of the intermediates and are characterized by one-electron transfer mechanism of inner-sphere nature. Again, the positive values of ΔG° obtained may confirm the non-spontaneity of the complexes formation in the rate-determining steps, as suggested by the cited proposed mechanisms. This means that the activated complexes could be more ordered and more compactness than that of the reactants which stabilized by a large solvation of the electron-transfer step. In addition, the non-dependency of the ionic strength of the rate constants may support this suggestion. But, this suggestion is not conclusive.

If the addition of Cl⁻ ions to the reaction mixture affected the rate-constant of the oxidation reaction, it means that [IrCl₆]²⁻ may be aquationed [40] as in Eq.(10),

\[
[\text{IrCl}_6]^{2-} + \text{H}_2\text{O} = [\text{IrCl}_3\text{H}_2\text{O}] + \text{Cl}^- \tag{10}
\]

It was found that the addition of Cl⁻ ions to the reaction mixture not affected the rate constants, therefore, this suggestions is neglected.

Again, addition of [IrCl₆]³⁻ product to the reaction mixture was found to has no effect on the reaction rates and, hence, this suggestion was excluded.

Furthermore, Moggi et al [43] showed that [IrCl₆]³⁻ is not appreciably photosensitive in the visible region (433 or 495 nm) although it is high photosensitive in the UV region (254 nm). Consequently photochemical induced reactions of [IrCl₆]³⁻ would not take place under the conditions used in the present work. Consequently, Eq. (6) can be considered as the sole rate-law expression for oxidation of MC by hexachloroiridate (IV).

The kinetic parameters of rate constants (k) of the elementary reaction were calculated from the temperature dependence of the rate constants from Eyring and Arrhenius equations. These values were calculated by the method of least-squares and are summarized in Table 3.

Oxidation of alcoholic groups is generally occurring by the rupture of either C-H or C-OH bond through transfer of hydride, proton or hydrogen atom in the rate determining step[44,45]. Transfer of hydride ion is usually accompanied by a simultaneous two-electron transfer in a single step. This transfer occurs in the redox reactions involving multi-equivalent oxidants of labile nature such as permanganate and chromate ions. Whereas, the transfer of hydrogen atom or protons may take place in redox reactions involving either inert oxidants such as hexachloroiridate (IV), hexacyanoferrate (III) or labile Ce(IV) of one-equivalent nature which tend to proceed by one-electron transfer mechanism.
Unfortunately, the rate-law expression here not provided any information on the nature of reaction mechanism whether is of outer- or inner-sphere nature. Therefore, some information may be gained from examining the magnitude of the rate constant and/or the magnitude of the entropy of activation. It has been reported [46,47] that the entropies of activation, \( \Delta S^\neq \), are negative for the oxidation reactions which are proceeding by inner-sphere mechanism; while the \( \Delta S^\neq \) for outer-sphere mechanisms tend to be of more positive values. Hence, two reaction mechanisms for formation of the intermediates may be considered, the first one being the transfer of electrons prior to the proton release. This mechanism corresponds to an outer-sphere type which proceeds by the formation of outer-ion sphere

\[
S + [\text{IrCl}_6]^{2-} \rightleftharpoons [s, [\text{IrCl}_6]^{2-}]
\]  

(11)

followed by electron-transfer, then the release of protons as follows,

\[
[S, [\text{IrCl}_6]^{2-}] \xrightarrow{\text{slow}} [S, [\text{IrCl}_6]^{3-}]
\]

(12)

\[
[S, [\text{IrCl}_6]^{3-}] \xrightarrow{\text{fast}} S + [\text{IrCl}_6]^{3-} + nH^+
\]

(13)

\[
S + [\text{IrCl}_6]^{2-} \xrightarrow{\text{fast}} \text{product} + [\text{IrCl}_6]^{3-}
\]

(14)

The second mechanism may involve the release of protons prior to the electron-transfer process which corresponds to the inner-sphere type as follows,

\[
S + [\text{IrCl}_6]^{2-} \rightleftharpoons [s, [\text{IrCl}_6]^{2-}]
\]

(15)

\[
[s, [\text{IrCl}_6]^{2-}] \rightleftharpoons [s, [\text{IrCl}_6]^{2-}] + nH^+
\]

(16)

\[
[S, [\text{IrCl}_6]^{3-}] \xrightarrow{\text{slow}} S + [\text{IrCl}_6]^{3-}
\]

(17)

\[
S + [\text{IrCl}_6]^{2-} \xrightarrow{\text{fast}} \text{product} + [\text{IrCl}_6]^{3-}
\]

(18)

The former mechanism seems likely to be assigned for the present investigation from thermodynamic points of view. Therefore, the inner-sphere mechanism may be considered as a more suitable one for oxidation of MC by hexachloroiridate (IV). This suggestion has been supported by the negative value observed for \( \Delta S^\neq \) (Table 3) along with the small values of the rate-constants of the elementary reaction (Table 2).

In view of the above kinetic interpretations and experimental observations a tentative reaction mechanism in good agreement with the kinetic results may be suggested by Scheme I.

Table 2. The rate constants (k) in the oxidation of methyl cellulose by hexachloroiridate (IV) in aqueous solutions. [\text{IrCl}_6]^{2-} = 2x10^{-4}, [\text{MC}] = 0.2 and I = 0.1 mol dm^{-3}.

| Constant | Temp, °C |
|----------|----------|
|          | 35°C     | 45°C     |
| 10^4, k  | 1.29     | 2.54     |

Table 3. Activation parameters of the rate constant (k) in the oxidation of methyl cellulose by hexachloroiridate (IV) in aqueous solutions.

| Parameters | \( \Delta H^\neq \) kJmol\(^{-1} \) | \( \Delta S^\neq \) Jmol\(^{-1}\)K\(^{-1} \) | \( \Delta G^\neq \) 313 kJmol\(^{-1} \) | \( E^\neq \) kJmol\(^{-1} \) |
|------------|-------------|-------------|---------------------------|-------------|
| k          | 54.24       | -127.36     | 92.19                     | 56.67       |
5. Conclusions

The kinetics and mechanism of oxidation of methyl cellulose (MC) by hexachloroiridate (IV) in aqueous perchlorate solutions have been investigated spectrophotometrically. Evidence for formation of 1:1 intermediate complexes prior to the rate-determining step was revealed. The reaction kinetics seems to be of considerable complexity where one chloride ion from hexachloroiridate (IV) oxidant may act as a bridging ligand between the oxidant and the substrate into the formed intermediate complex. The kinetic observation indicated that this redox reaction proceeds by one-electron transfer mechanism of inner-sphere nature.

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