Oxidation of chromium (III) by periodate in aqueous alkaline medium 
- A kinetic study

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The kinetics of oxidation of chromium(III) by periodate in aqueous alkaline medium at 27°C obeys the rate law

$$\frac{d[Cr(III)]}{dt} = [Cr(III)][I(VII)] \left\{ \frac{k_1 + \frac{k_2 K_w}{K_i[OH^-]}}{K_i} \right\}$$

where $K_i$ is dissociation constant of the equilibrium $H_2IO_7^2-$ $\leftrightarrow$ $HIO_4^-+H_2O$, $k_1$ and $k_2$ are the rate constants for the slow steps of the reactions $H_2IO_7^2-$ $\rightarrow$ $Cr(OH)_4^{2-}$ and $HIO_4^-+Cr(OH)_4^{2-}$ respectively. The constants $k_1$ and $k_2$ are calculated and used to regenerate the experimental rate constants at various conditions.

The periodate ion has been extensively used in oxidation of organic compounds, particularly in the oxidation of glycols. The mechanism of oxidation of 1,2-diols by periodate has been shown to proceed by the way of covalent link involving a cyclic intermediate. This corresponds to an inner-sphere mechanism. However, the literature on the mechanism of oxidation reactions of inorganic materials by periodate is scanty.

The kinetics of oxidation of chromium(III) in alkaline medium has been studied with a few oxidants. The results of studies, in particular the nature of reactive chromium(III) ion, has kindled a further interest in alkaline chromium(III) chemistry. As the reduction potentials of couples $Cr(VI)/Cr(III)$ and $IO_4^-/IO_3^-$ are -0.13 V and +0.70 V respectively at pH > 12, the title reaction is feasible. Oxidation of chromium(III) by periodate has been studied in acidic media, where the second order dependence on chromium(III) and first order on periodate was observed. The present investigation of the same reaction in alkaline media is different and hence the title study to understand the alkaline chemistry of chromium (III) and periodate.

Materials and Methods
Reagent grade chemicals and doubly distilled $H_2O$ were used throughout. A stock solution of periodate was prepared by dissolving a known mass of $KIO_4$ in $H_2O$ and stored in a vessel wrapped with aluminum foil to avoid photochemical reaction. The solution was standardised iodometrically at neutral pH. The chromium (III) solution for every kinetic run was prepared freshly from recrystallised $K_2Cr_2(SO_4)_3$ in $H_2O$ and was standardised by oxidation to chromium(VI) with silver(I) in acidic medium. The chromium(III) solution at pH > 12 was clear when freshly prepared, and turbidity meter indicating the homogeneity of solution up to ca. 40 h. Chromium(VI) and iodate solutions were prepared by dissolving $K_2Cr_2O_7$ and $KIO_4$ in water respectively. $NaClO_4$ and $NaOH$ were used to adjust the ionic strength and alkalinity respectively, to the required values.

Kinetic studies
Kinetic runs were followed using equivalent concentrations of reactants at 27 ± 0.1°C unless otherwise stated. The reaction was initiated by mixing the freshly prepared chromium(III) solution to the thermally equilibrated periodate solution which also contained the required quantity of sodium hydroxide and sodium perchlorate to maintain alkalinity and ionic strength constant respectively. The progress of the reaction was monitored by measuring the absorbance of one of the products, chromium(VI) in the reaction solution in a 1 cm cell with a thermostated compartment of a Hitachi 150-20 spectrophotometer coupled with HI-Tech (SFA-12) Rapid Kinetic Accessory at 372 nm ($c = 4670 \pm 2 \% dm^3 mol^{-1} cm^{-1}$) where the other species in the mixture do not absorb significantly. The concentration of chromium(III) at any time was obtained by
accounting for the chromium(VI) concentration. The kinetic runs were reproducible within ± 5%.

Second order rate constant (k_S) were obtained at equivalent concentrations of chromium(III) and periodate from a plot of 1/[Cr(III)] versus time. Such plots were linear up to two half lives completion of the reaction and k_S values were reproducible within ± 5%. While varying the concentrations of chromium(III) and periodate, initial rates were also obtained [chromium(VI)] vs. time plots, by plane mirror method. Runs under conditions of pH greater than 12 lead to satisfactory results. However, at lower [OH−] of around less than 0.05 mol dm−3, the reaction mixture tended to become turbid presumably due to the precipitation of chromium(III) hydroxide, Cr(OH)₃. Hence, solubility of chromium(III) had been tested with a Systronic Nephelo Turbidity Meter-131 and pH meter. And also in view of the tendency of chromium(III) solution to undergo precipitation after standing for 36 hours as tested by Nephelo Turbidity meter, the runs were restricted to freshly prepared solutions. It may be noted that the onset of slow precipitation starts after about 40 hours. However, the kinetics was also studied for aged chromium(III) solution i.e. before getting the precipitation. It was observed that the orders in oxidant, reductant and alkali concentrations remain the same, except that the marginal decrease in second order rate constant, k_S with ageing of chromium(III) solution.

Use of polythene / acrylic ware and quartz or polyacrylate cells gave the same results as with the glass vessels and cells, indicating that the surfaces play no important role on the reaction rate. The effect of dissolved oxygen on the rate of reaction was checked by preparing reaction mixture and following the reaction in the atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed. In view of the ubiquitous contamination of carbonate in basic solution the effect of carbonate on the reaction was also studied. Added carbonate up to 1.0 mol dm−3 showed no effect on the reaction rate. However, the second order rate constant, k_S decreased with the decrease in the dielectric constant of the medium. A plot of log k_S versus 1/D was linear with negative slope.

Effect of added products
Initially added products, chromium(VI) and iodate in the concentration range of 2.0 × 10⁻⁴ to 1.0 × 10⁻⁴ mol dm⁻³ all other concentrations being constant did not have significant effect on the reaction rate.

Effect of varying ionic strength and dielectric constant
The ionic strength of the reaction medium was varied from 0.5 to 2.0 mol dm⁻³ with NaClO₃ at fixed [reactants] and [alkali]. The results showed that ionic strength did not have any significant effect on the reaction. Likewise the dielectric constant (D) of the reaction medium was varied by varying the content of i-butanol with water which is inert towards oxidant. The second order rate constant, k_S decreased with the decrease in the dielectric constant of the medium. A plot of log k_S versus 1/D was linear with negative slope.

Effect of temperature
It has been reported in the case of oxidation of chromium(III) by hexacyanoferrate(III) in alkali, the rate of reaction decreased with increase in temperature. However, for periodate oxidation, rate increased with increase in temperature. The temperature effect was studied at 27, 32, 37, 42 and 47°C at fixed [reactants], [alkali] and ionic strength and from the plot of log k_S versus 1/T, the activation parameters of the reaction were obtained as Ea = 89 ± 2 kJ mol⁻¹, log A = 16.5 ± 0.5, ΔS_A = - 64 ± 4 J K⁻¹ mol⁻¹, ΔH_A = 84 ± 2 kJ mol⁻¹ and ΔG_A = 103 ± 2 kJ mol⁻¹.

Discussion
In alkaline medium, the results obtained are different from what were obtained in aqueous acidic medium. In acidic media, order in [chromium(III)] was two, [periodate], one and
reaction was inverse dependent on [H⁺]. The inverse [H⁺] dependence has been explained by considering the deprotonated periodate as active species which would be present in acidic medium. Whereas in the present study the order in [chromium(III)] and [periodate] is unity each and it is inverse fractional in [alkali].

In aqueous alkaline medium, the periodate exists in four forms, IO₄⁻, H₂IO₄⁻, HIO₄⁻ and dimeric form, H₂IO₄⁺. Among these, H₂IO₄⁻ and HIO₄⁻ are hydroxyspecies, which are in equilibrium as in Eq. (2).

\[ \text{H}_2\text{IO}_4^- \leftrightarrow \text{H}_2\text{IO}_4^+ + \text{H}^+ ; K_1 = 2.5 \times 10^{-11} \] (2)

The unprotonated periodate, IO₄⁻ exists mostly at neutral pH and dimeric form, H₂IO₄⁺ is known to be present at very high [alkali]. Hence, it is possible to conclude that under the conditions of pH employed viz., [OH⁻] = 0.50 mol dm⁻³, the periodate may exist as H₂IO₄⁻ and HIO₄⁻ which can be considered as prime active species. As for the reductant, chromium(III), the species Cr(OH)₃⁺, Cr(OH)₂⁺, hydrolytic oligomers, Cr(OH), and Cr(OH)₄⁻ in addition to higher polymers are known to exist in aqueous solution. In acidic media, Cr(OH)₃⁺, Cr(OH)₂⁺ and hydrolytic oligomers exist in the pH range 7 to 10, Cr(OH)₃ is known to exist in solid state. Chromium(III) exhibits greater solubility at higher pH by its amphoterism due to the predominance of species Cr(OH)₄⁻. The polymeric species are formed only on long standing. Hence the active species of Cr(III) in soluble form at alkaline medium is considered to be as Cr(OH)₄⁻ and also the pH employed in this study, reveals the existence of Cr(III) completely as Cr(OH)₃⁺.

A mechanism with oxidant species, H₂IO₄⁻ and HIO₄⁻ and reductant, Cr(OH)₄⁻ can account for the experimental results as in Scheme 1 where H₂IO₄⁻ and HIO₄⁻ exist in equilibrium step (2). These two interact with Cr(OH)₄⁻ in two different slow steps (3) and (4) to yield Cr(IV) and I(VI) species and followed by other fast steps to give the products of the reaction.

The rate law of the Scheme 1 can be derived from the combined slow steps (3) and (4).

\[ \frac{d[\text{Cr(III)}]}{dt} = \frac{k_1 \text{[H}_2\text{IO}_4^- \text{]} [\text{Cr(III)}] + k_2 \text{[H}_3\text{IO}_4^- \text{]} [\text{Cr(III)}]}{K_w} \] (11)

From Eq. (2) the rate law (10) becomes (11).

\[ \frac{d[\text{Cr(III)}]}{dt} = \frac{[\text{Cr(III)}][I(VI)]}{K_i} \left( k_1 + k_2 K_w \right) \] (11)
where \( k_1 \) and \( k_2 \) represent the rate constants for the slow steps (3) and (4) respectively. \( K_w \) is the dissociation constant of \( \text{eq} (2) \) and \( K_\text{OH}^- \) is the ionic product of water. It may be noted that \( I(VII) \) oxidation of \( \text{Cr(III)} \) takes place with single electron transfer in rate determining steps (3) and (4) which is in accordance with well-accepted principle\(^{15}\). It explains the order of unity each in oxidant and reductant. Besides these, some other reactions in the fast steps are taking place involving \( \text{Cr(IV)} \), \( \text{Cr(V)} \) and \( \text{I(VI)} \) intermediates. In acidic media, chromium(V) is relatively stable and its ESR spectrum has been recorded\(^{15}\); chromium(IV) is the one of the most potent oxidants known in the acidic media\(^{14}\) and can oxidise manganese(II) to manganese(III). Chromium(VI) itself loses much of its oxidising capacity in alkaline media as evidenced by reduction potential\(^{9}\) and this trend appears to apply to its lower oxidation states as well. The results of this study reveal that these chromium species are much weaker oxidants in alkaline medium. The mechanism shown in Scheme 1 and rate law (11) may be verified in the form of equation (12) by plotting \( k_i \) versus \( 1/\text{[OH}^-] \). The plot should be linear as shown in Fig. 1.

\[
k_i = k_1 + \frac{k_2 K_w}{K_{\text{OH}^-}} \quad \ldots (12)
\]

The slope and intercept of such plot lead to the values of \( k_1 = 14 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) and \( k_2 = 1.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). Using these constants and the \( K_{\text{OH}^-} = 2.5 \times 10^{-12} \) from the reported value, the rate constants are regenerated (Table 1).

It has been reported\(^{19}\) that the periodate exists in dimeric form in its higher concentration which is also true for the higher concentration of alkali. Hence the study is restricted to the second order conditions of low concentrations. The increase in rate with increase in dielectric constant of reaction medium is qualitatively expected from the above mechanism where, ions of like charges interact in the slow steps. Since both the \( \text{Cr(OH)}_4^+ \) and \( \text{H}_2\text{IO}_6^2- \) or \( \text{H}_2\text{IO}_6^+ \) are reactive species, the electron transfer may take place via inner-sphere mechanism, through the common bridging ligand \( \text{OH}^- \) group or through the hydroxo-chromium to oxygen-iodine. Hence there may be negligible effect of ionic strength; abnormally large value of observed second order rate constants and relatively high value of apparent entropy of activation. This has also been supported by earlier work\(^{16}\).

Inverse dependence of reaction rate on \( [\text{OH}^-] \) may be due to the involvement of oxidant species, periodate (Eq.2) in two forms viz. \( \text{H}_2\text{IO}_6^2- \) and \( \text{H}_2\text{IO}_6^+ \), which are involved in the slow steps of reaction as shown in Scheme 1 in which the negatively charged chromium(III) species and periodate species as well as the oxygen-iodine bond being weakened which facilitates the transfer of electron or transfer of oxygen atom in opposite direction.

References