Kinetics & Mechanism of Oxidation of Potassium Thiocyanate by Potassium Bis(tellurato)cuprate(III)

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Potassium bis(tellurato)cuprate(III) oxidises potassium thiocyanate to CN⁻ and SO₄²⁻. The reaction is retarded by OH⁻ and added tellurate ion. The kinetics is observed to be complicated and a suitable rate equation has been derived consistent with kinetic data. The oxidation presumably involves electron transfer occurring through an inner sphere complex of Cu(III) with CNS⁻.

The kinetics of oxidation of several substrates by copper(III) stabilised in the form of anionic complexes such as with peptides¹⁻³, dimethylglyoxime⁴ and imine oximes⁵⁻⁶ have been investigated by several groups of workers. The only inorganic ligands used to stabilise copper(III) are periodate and tellurate ions in the alkaline medium⁷ and the structures of tellurate and periodate complexes have been established⁸. Earlier we have reported on the kinetics of oxidation of ketones⁹ and that of nitrophenol¹⁰ by potassium bis(tellurato)cuprate(III) in aqueous alkaline medium. The title investigation is an extension of our earlier work.

Materials and Methods

All the chemicals used were of either AR or proanalysi grade. The stock solution of potassium bis(tellurato)cuprate(III) was prepared and standardised by the procedure of Chandra and Yadava¹¹. The solution was stable when preserved in a refrigerator. Potassium thiocyanate solution was always prepared fresh and standardised by Volhard's method. A solution containing appropriate amounts of KCNS, KOH, potassium tellurate and KNO₃ (to maintain constant ionic strength) and a solution of the oxidant were thermally equilibrated separately at 30°C (±0.2°C) for 1 hr and then mixed thoroughly. The progress of the reaction was followed spectrophotometrically at 415 nm using a Zeiss VSU 2p UV-visible spectrophotometer fitted with a cell holder through which water from a thermostat was circulated to maintain the desired temperature. Quartz cells of 10 mm path length were used. The hydroxide ion concentration in the reaction mixtures, determined by acidimetry before and after completion of the reaction, remained practically constant during the period of the reaction. The self-decomposition of Cu(III) was routinely checked and found to be negligible. The rate constants reported here are averages of at least three independent runs.

Results and Discussion

Potassium thiocyanate was found to be smoothly oxidised by potassium bis(tellurato)cuprate(III) in aqueous alkaline medium to afford SO₄²⁻ and CN⁻ as the main products. The disappearance of Cu(III) under pseudo-first order conditions (at least ten-fold excess of CNS⁻) is mostly first order as demonstrated by the linearity of log(absorbance) versus time plots. The deviation from linearity at the initial stages might be due to either a small induction period or autocatalytic nature of the reaction. The pseudo-first order rate constants were computed from the slopes of the above plots. When the initial [oxidant] was varied keeping the concentration of other reactant species, ionic strength etc. constant, log (absorbance) versus time plots were parallel and kobs values remained constant proving that the order in Cu(III) is unity. The pseudo-first order rate constants increased with increase in [CNS⁻] at fixed concentrations of other reactants and fixed ionic strength, but kobs/[CNS⁻] values decreased. Plot of 1/kobs versus 1/[CNS⁻] is linear (Fig. 1) with a positive slope and intercept.

Unlike oxidation of ketones⁹ by potassium bis(tellurato)cuprate(III), oxidation rate of CNS⁻ decreased with increase in [OH⁻]. Plot of kobs⁻¹ versus [OH⁻] is linear (Fig. 2) giving the following rate equation with respect to [OH⁻].

\[ k_{obs}^{-1} = a + b[OH^-] \]  \( \ldots (1) \)

As several ionic equilibria with the oxidant are involved, it is essential to study the effect of [tellurate] on the rate of oxidation of CNS⁻. The rate at constant [OH⁻] and ionic strength decreased with increase in [tellurate]. The plot of kobs versus 1/[tellurate] is linear (Fig. 3) with a positive slope and intercept consistent with rate equation of the type.
Fig. 1—Plot of 1/k_{obs} versus 1/[CNS⁻], ([Cu³⁺]) = 1.22 × 10^{-4} mol dm⁻³; μ = 0.5, temp. = 30°C; [OH⁻] = (a) 0.42 mol dm⁻³, (b) 0.087 mol dm⁻³.

\[ k_{obs} = p + q / [\text{tellurate}] \]  

where \( p \) and \( q \) are constants.

The rate of oxidation of CNS⁻ is not affected by change in ionic strength suggesting that the rate-limiting step in the reaction may involve an ion and neutral molecule.

**Rate law and mechanism**

Movious while studying the oxidation of alcohols by bis(periodato)cuprate(III) observed direct dependence of rate in [OH⁻] and proposed ionisation of the oxidant to afford a deprotonated monoiodato complex of copper(III), which acted as the active oxidant species. But in the oxidation of CNS⁻, the situation appears to be different since the oxidation shows inverse dependence on [OH⁻]. The following mechanism (Scheme 1) is consistent with the experimental observations:

\[
\begin{align*}
[Cu(HL)]^5^- & \rightleftharpoons [Cu(HL)]^1^- + -HL^4- \quad (i) \\
[Cu(HL)]^5^- + OH^- & \rightleftharpoons [Cu(OH)(HL)]^3^- + [HL^4-] \quad (ii) \\
[Cu(HL)]^1^- + CNS^- & \rightleftharpoons \text{Complex (1) \ (C₁)} \quad (iii) \\
[Cu(HL)]^5^- + CNS^- & \rightleftharpoons \text{Complex (2) \ (C₂)} \quad (iv) \\
\text{Complex (C₁)} & \rightarrow CN^- + SO_4^{2-} + Cu(II) \quad (v) \\
\text{Complex (C₂)} & \rightarrow CN^- + SO_4^{2-} + Cu(II) \quad (vi)
\end{align*}
\]

**Scheme 1**

In Scheme 1 \([Cu(HL)]^5^-\) is the bis(tellurate)cuprate(III) anion and \([HL]^4^-\) is the deprotonated tellurate ion, i.e. \([H_2TeO_6]^4^-\).
Scheme 1 will lead to the following rate expression

\[
k_{\text{obs}} = \frac{k_1K_3K_1[\text{CNS}^-] + k_2K_4[\text{CNS}^-][\text{HL}^4^-]}{[(\text{HL}^4^-) + K_1 + K_2[\text{OH}^-] + K_1K_3[\text{CNS}^-] + k_4[\text{CNS}^-][\text{HL}^4^-]]}
\]  

(7)

The following limiting cases of this equation will be of interest. (a) In the presence of excess of [\text{HL}^4^-] it can be presumed that [\text{HL}^4^-] > > (K_1 + K_2[\text{OH}^-] + K_1K_3[\text{CNS}^-] + K_4[\text{CNS}^-][\text{HL}^4^-]) then Eq. (7) reduces to,

\[
k_{\text{obs}} = \frac{k_1K_1K_3[\text{CNS}^-] + k_2K_4[\text{CNS}^-][\text{HL}^4^-]}{[\text{HL}^4^-]}
\]  

(8)

(b) If we assume that \(K_4[\text{CNS}^-][\text{HL}^4^-]\) is negligible compared to all other terms, Eq. (7) leads to Eq. (10).

\[
k_{\text{obs}} = \frac{kK_3K_1[\text{CNS}^-]}{[\text{HL}^4^-] + K_1 + K_2[\text{OH}^-] + K_1K_3[\text{CNS}^-]} \quad \cdots \quad (9)
\]

or

\[
k_{\text{obs}}^{-1} = \frac{K_2[\text{OH}^-] + K_1 + [\text{HL}^4^-]}{k_1K_3K_1[\text{CNS}^-]} + \frac{1}{k_1} \quad \cdots \quad (10)
\]

At high [\text{OH}^-], \(K_1 + [\text{HL}^4^-]\) can be safely assumed to be smaller than \(k_3[\text{OH}^-]\) and hence negligible. Eq. (10) would then take the form,

\[
1/k_{\text{obs}} = \frac{K_2[\text{OH}^-]}{k_1K_3K_1[\text{CNS}^-]} + \frac{1}{k_1}
\]  

(11)

In the presence of constant [\text{CNS}^-] the plot of \(1/k_{\text{obs}}\) versus [\text{OH}^-] is found to be linear with an intercept and slope, thereby confirming the applicability of the rate law (11) and providing justification for the assumptions. From the intercept of the plot \(k_1\) is found to be 800. Substituting the value of \(k_1\) in the slope the value of \(K_2/K_3K_1\) is calculated to be 0.0385.

Similarly at constant [\text{OH}^-], the plot of \(1/k_{\text{obs}}\) against \(1/[\text{CNS}^-]\) is predicted by Eq. (11) to be linear which in fact is the case. Further the value of \(k_1\) as obtained from the intercept of this plot should be identical with the \(k_1\) obtained from the intercept of the \(1/k_{\text{obs}}\) versus [\text{OH}^-] plot at constant [\text{CNS}^-]. An examination of the \(k_1\) values obtained from [substrate] and [\text{OH}^-] variations are respectively \(1.48 \times 10^{-3}\) and \(1.25 \times 10^{-3}\). From the slope and intercept of the plot of \(1/k_{\text{obs}}\) versus \(1/[\text{substrate}]\), \(K_2/K_3K_1\) has been calculated to be 0.0374, which is almost similar to the value of 0.0385 obtained from the slope and intercept of \(1/k_{\text{obs}}\) versus [\text{OH}^-] plot. The close agreement between \(K_2/K_3K_1\) values from different sets of data confirm the mechanism given in Scheme 1.

Oxidations by Cu(III) have been well established by several workers to proceed by one electron transfer. In the present case it is now certain that...
CNS⁻ oxidation by bis(tellurato)cuprate(III) occurs through the reversible formation of an intermediate or a complex preceding the rate limiting decomposition step. The initial complex is probably formed by the axial coordination of CNS⁻ with Cu(III) which facilitates electron transfer from CNS⁻ to Cu(III) resulting in the formation of a radical. Sulfab and coworkers⁶ have also proposed an inner sphere complex of Cu(III) with the iodide weakly coordinated in an axial position⁶ in the oxidation of iodide. The rapid rates of oxidation of [IrCl₆]⁻³(Ref. 15) and [Fe(CN)₆]⁴⁻(Ref. 16) by Cu(III) have been similarly attributed to axial bridging which helps to form the inner sphere complex by concomitant electron transfer.

References