Kinetics and mechanism of oxidations of [N-(2-hydroxyethyl)
ethylene-diamine-N,N',N'-triacetato] chromium (III) by N- bromosuccinimide

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The kinetics of oxidation of [N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetato] chromium (III) complex [Cr(III)(H2O)(TOH)] by N-bromosuccinimide (NBS) in aqueous solution to yield chromium (IV) has been studied spectrophotometrically at 20-40°C range. The reaction is first order each in [NBS] and [Cr(III)], and the rate increases with increase in pH between 6.30 and 7.33. The thermodynamic activation parameters have been calculated. The experimental rate law is consistent with a mechanism in which the deprotonated [Cr(III)(OH)(TOH)]+ is considered to be the most reactive species compared to its conjugate acid. It is assumed that electron transfer takes place via an inner-sphere mechanism.

N-Bromosuccinimide (NBS) has been used on a large-scale as a brominating and oxidizing agent for organic compounds, but its use to oxidize inorganic compounds has received little attention. NBS has been used to oxidize cobalt complexes. Oxidation of [Co(III)EDTA]2-5 (EDTA = ethylene diamine tetraacetic acid) and Co(II)EDTA 9 (HEDTA) = N-(2-hydroxyethyl)ethylene diamine-N,N',N'-triacetate) by NBS in aqueous solution was investigated. It was found that these reactions proceed via inner sphere mechanism. The detection of initial cobalt (III) products, which are slowly converted into the final cobalt (III) products, supports this mechanism. Also, oxidation of chromium (III) complexes by NBS was studied. In the oxidation of [Cr(EDTA)] by NBS in aqueous solution, it was assumed that the electron transfer took place through an inner-sphere mechanism with the hydroxo ligand of the chromium (III) complex bridging the two reactants. Oxidation of [Cr(H2O)6]3+ (ref. 8) and [Cr(en)2(H2O)2]3+ (ref. 9) by NBS was also studied. The reaction was found to proceed via a mechanism in which coordinated water was replaced by NBS prior to electron transfer.

The kinetics of oxidation of [Cr(L2)(H2O)]3+ (L = 2-amino methylpyridine by NBS has been studied and it is assumed that electron transfer takes place via an inner sphere mechanism and the deprotonated [Cr(L2)(OH)]3+ is considered to be the most reactive species compared to its conjugate acid.

In this paper kinetics of the oxidation of [Cr(III)(H2O)(TOH)] [TOH = N-(2-hydroxyethyl)ethylene diamine-N,N',N'-triacetate] is reported in order to study the effect of complex formation on the resistance of chromium (III) towards oxidation.

Materials and Methods

[Cr(III)(H2O)(TOH)] was prepared by the method of Wharton and Sykes. Reagent grade chemicals were used without further purification. NaOH, NaNO3 and NaH2PO4 solutions were prepared by weight. A stock solution NaOH was standardized against standard HCl. NaH2PO4/NaOH buffers of known pH (6.30 - 7.33) were used, and their ionic strengths were adjusted with NaNO3. Freshly prepared solutions of NBS (Aldrich) were used.

Kinetic procedures

The UV-vis-absorption spectra of products of oxidation of [Cr(III)(H2O)(TOH)] by NBS, in the presence of NaOH/NaH2PO4 buffer, were recorded on a Shimadzu UV-160 IPC spectrophotometer. Initial oxidation rates were measured by monitoring the absorbance of chromium (VI) at 372 nm. A Milton and Roy SP 601 spectrophotometer was used for this purpose. All reactants, except NBS, were equili-
Oxidation products

UV-vis is absorption spectra for the reaction mixture, Fig. 1, reveal that the characteristic peaks for chromium (III) at 570 and 378 nm disappeared and a new peak at 372 nm with molar absorption coefficient $\epsilon_{372} = 4576 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ appeared (as the experimental value determined for chromate ion at the same $pH$). The UV-vis is spectra of the final product is the same as that of chromate ion at the same $pH$. This is an evidence that Cr(VI) is the essential product of the oxidation of [Cr$^{III}$(H$_2$O)(TOH)] complex.

Stoichiometry of the reaction

The stoichiometry of the reaction was calculated by measuring the absorbance of chromium (VI) produced from a reaction mixture containing a known excess of [Cr$^{III}$] complex over that of [NBS] at $\lambda_{372}$.

Results and Discussion

The overall stoichiometry for the reaction was found to be $2.9 \pm 0.1$ mole of NBS for 1 mole of chromium (III) complex during the kinetic measurements. The reaction may be represented stoichiometrically by Eq. (1).

$$\text{Cr}^{III} + 3 \text{NBS} \rightarrow \text{Cr}^{VI} + 3\text{Br}^- + \text{other products} \quad \ldots(1)$$

Plots of $\ln(A_\infty - A_t)$ versus time and $1/(A_\infty - A_t)$ versus time, where $A_t$ and $A_\infty$ are absorbances at time $t$ and at infinity respectively, showed marked deviations from linearity. The order in the complex is thus neither first nor second. The initial rate method was thus employed to determine the order in the [complex]. The initial rate, $d[\text{Cr}^{VI}]/dt$, was calculated by dividing the slope of the initial tangents of these plots by the calculated molar absorptivity $\varepsilon$ of chromium (VI) and the $pH$ used. Pseudo-first order rate constants, $k_{obs}$, were calculated by dividing the initial rate by initial [Cr$^{III}$].

The initial rate method was preferred so as to avoid difficulties in monitoring reversible equilibria and to eliminate complications from side or subsequent steps.

The side or subsequent steps which may be encountered include possible reduction of the oxidized chromium (VI) by the accumulated Br$^-$; in addition, the succinimidyl radical will prefer to abstract a hydrogen atom from the solvent to form succinimide rather than dimerize to bisuccinimidyl$^{12,13}$ which may lead to perturbation of the chemical equilibrium by a change in $pH$. Also, when the rate is measured at the start of the reaction, it can be assumed that complications caused by all backward reactions do not occur.

The constancy of $k_{obs}(4.31 \pm 0.02 \times 10^{-4} \text{ s}^{-1})$ over the [complex] range of (3.0-10.0) $\times 10^{-4}$ mol dm$^{-3}$ under fixed experimental conditions ($T = 30^\circ C$, $pH = 7.33$, $I = 0.2$ mol dm$^{-3}$) is in agreement with a first order dependence on its concentration. At constant $[H^+]$ and ionic strength, $1/k_{obs}$ varies linearly with $1/[\text{NBS}]$ at different temperatures with correlation.
The experimental rate equation suggests that a fast equilibrium step precedes the slow intramolecular electron transfer step. A possible mechanism is described by Eqs (5-12)

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egin{align*}
\text{[Cr}^{II} (\text{H}_2\text{O})(\text{TOH})] & \rightarrow \text{[Cr}^{II} (\text{OH})(\text{TOH}))^- + \text{H}^+ \quad K_1 \\
\text{[Cr}^{II} (\text{H}_2\text{O})(\text{TOH})] + \text{NBS} & \rightarrow [\text{TOH} \text{Cr}^{III} (\text{NBS})] + \text{H}_2\text{O} \quad \ldots (5) \\
\text{[Cr}^{III} (\text{OH})(\text{TOH})] + \text{NBS} & \rightarrow [\text{TOH} \text{Cr}^{III} (\text{OH})(\text{NBS})^-] \quad \ldots (6)
\end{align*}
\]

\[
egin{align*}
(\text{TOH}) \text{Cr}^{III} (\text{NBS}) & \rightarrow [(\text{TOH}) \text{Cr}^{IV} (\text{OH})] + \text{Br} + \text{R} \quad \ldots (7) \\
(\text{TOH}) \text{Cr}^{IV} (\text{OH}) & \rightarrow \text{Cr}^{IV} + \text{TOH} \quad \ldots (8) \\
\text{Cr}^{IV} + \text{R} & \rightarrow \text{Cr}^{V} + \text{R}^\Sigma \quad \ldots (9) \\
\text{Cr}^{V} + \text{R} & \rightarrow \text{Cr}^{VI} + \text{R}^- \quad \ldots (10)
\end{align*}
\]

with \( K_1 \) and \( K_2 \) having values of \( 3.63 \times 10^{-7} \) mol dm\(^{-3}\) and \( 1.58 \times 10^{-10} \) mol dm\(^{-3}\) respectively at 25°C and \( I = 0.1 \) mol dm\(^{-3}\). It is clear from the value of \( K_2 \) that \([\text{Cr}^{III} (\text{OH})(\text{TOH})]^-\) was not present at the employed \( p\)H value at the present study. The species present at low \( p\)H has the ligand bound in quinquedentate manner, with the (2-hydroxy ethyl) group uncoordinated. The absence of an acid dissociation constant at \( pK_a \approx 3 \) precludes the presence of any uncomplexed \(-\text{COO}^-\) groups.
Since $[\text{OH}^-]$ is a better bridging ligand than $\text{H}_2\text{O}$, $(\text{TOH})\text{Cr}^{III}$ $(\text{OH})(\text{NBS})$ is a more reactive species than $(\text{TOH})\text{Cr}^{III}$ $(\text{NBS})$. Thus, we can assume that $k_2 K_1 K_4 > k_1 K_3 [H^+]$ and Eq. (17) reduces to,

$$k_{\text{obs}} = k_2 K_4 [\text{NBS}]/(1 + k_1 [H^+] + [\text{NBS}])$$

(18)

On rearranging,

$$1/k_{\text{obs}} = 1/[\text{NBS}] [(H^+] + K_1)/k_2 K_4 + K_3$$

(19)

At constant $[H^+]$, Eq. 19 is consistent with the experimental rate law shown in Eq. 2 where $a = k_2 K_1 K_4 / [H^+]$ and $b = (K_3 [H^+] + K_1 K_4) / K_1 + [H^+]$. Plots of both $1/a$

$$K_1 + [H^+] / K_2 K_4$$

and $b/a = (K_3 [H^+] + K_1 K_4) / K_1 + [H^+]$. 

$k_2 K_1 K_4$ versus $[H^+]$ are linear with correlation coefficients $r = 0.9982$ and 0.9918, respectively. Value of $K_1$ was calculated by dividing the intercept by the slope of the plot of $1/a$ versus $[H^+]$ as $1.21 \times 10^{-7}$ mol dm$^{-3}$ at 30°C. The intramolecular electron transfer rate constant, $k_2$, was calculated from the intercept of a plot of $b/a$ versus $[H^+]$ as $1.28 \times 10^{-3}$ s$^{-1}$ at 30°C. The value of $K_3$ was calculated by dividing the slope of both $b/a$ by $1/a$ versus $[H^+]$ as $18.433$ mol dm$^{-3}$ at 30°C. Substitution the value of $k_2$ gives $K_2$ from the intercept of a plot of $1/a$ versus $[H^+]$ as $35.062$ mol dm$^{-3}$ at 30°C.

The intramolecular electron transfer step is endothermic as indicated by the positive $\Delta H^\circ$ value.

Thermodynamic activation parameters associated with $k_2$ obtained from a least squares fit to transition state theory equation are $\Delta H = 81.2$ kJ mol$^{-1}$ and $\Delta S = -31.5$ JK$^{-1}$ mol$^{-1}$.

The small negative $\Delta S$ value for a redox reaction between an ion and a neutral molecule has been suggested to be largely the result of the slightly higher charge concentration on encounter complex, which causes a significant ordering of the solvated water molecules.

From the above discussion, an inner sphere mechanism is proposed for the oxidation of $\text{Cr}^{III}$ $(\text{H}_2\text{O})(\text{TOH})$ by NBS in which the $\text{Cr}^{III}$ $(\text{OH})(\text{TOH})$ is bridged to NBS through a bridging hydroxo ligand. Evidence for this mechanism is provided by the following observations: (i) the coordination of NBS to the metal is most probably through the carbonyl group; (ii) the hydroxo-ligand can act as ligand bridges as in $\text{[Co(EDTA)(OH)]}^3$ (ref. 5) and $\text{[Cr(EDTA)(OH)]}^2$ (ref. 7) (iii) the inverse dependence on $[\text{H}^+]$ is usually ascribed to oxidation of the hydroxo species to give very effective OH bridging in an inner-sphere process and (iv) no reaction was observed at $p\text{H} < 6$ where the hydroxo-species is not present.

References