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Kinetics of the Oxidation of [*N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetato]chromium(III) by Periodate

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The kinetics of oxidation of $[Cr^{III}(H_2O)(TOH)]$, (TOH=*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetate) by periodate in aqueous solutions has been found to obey the following equation

$$\text{Rate} = \frac{k_2K_6[Cr^{III}]_T\,[I^{VII}]_T}{1+[H^+]/K_5+K_6[I^{VII}]_T}$$

where k_2 is the rate constant for the electron-transfer process, K_5 is the equilibrium constant for dissociation of $[Cr^{III}(H_2O)(TOH)]$ to $[Cr^{III}(OH)(TOH)]^-+H^+$ and K_6 is the pre-equilibrium formation constant. The activation parameters are reported. It is proposed that electron transfer proceeds via an innersphere mechanism with the hydroxo ligand of the chromium(III) complex bridging the two reactants.

Metal complexes, which are relatively easily oxidized by IO_4^- in aqueous solution, seem to fall into one of two classes: (i) labile complexes[1—6] or (ii) inert complexes that can offer a bridging ligand.[7,8] The mechanism of oxidation of the labile complexes is believed to be of the innersphere type, and in several cases direct evidence in support of this mechanism has been presented.[2—6] Substitution into the inner coordination sphere of the IO_4^- ion, which is labile, is likely.[9] In case of oxidation of $[Cr^{III}(edta)(H_2O)]$ by periodate,[6] it was proposed that the oxidation may proceed via one- or two-electron transfer giving Cr(IV) or Cr(V), respectively, in the rate-determining step, followed by a fast step leading to Cr(VI). An innersphere process is also believed to be operating in the oxidation of inert complexes.[7,8] The unusual second-order dependence on $[Cr(H_2O)_6]^{3+}$ in the chromium(III)-periodate reaction seems to support an innersphere mechanism.[7] The two electron transfer step proposed for this reaction requires this mechanism,[10] where the hydroxo form, $[CrOH]^{2+}$, was considered to be the reactive chromium(III) species.

In particular we have chosen the edta analogues in that it can be supported that some properties of the respective complexes are influenced by the position and number of the functional groups. In this study the kinetics of oxidation of $[Cr^{III}(H_2O)(TOH)]$, where TOH is *N*-(2-hydroxyethyl)ethylenediaminetriacetate, is reported.

Experimental

Reagents. Reagent grade *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetic acid, sodium periodate, chromium(III) nitrate hexahydrate, sodium dihydrogenphosphate, sodium hydroxide, and sodium nitrate were used without further purification. Solution of $[Cr^{III}(H_2O)(TOH)]$ was prepared by the method of Wharton and Sykes.[11] Molar absorption coefficients of this complex were calculated on the basis of the chromium concentration which was determined spectrophotometrically as chromate.[12] At the range of pH 6.1—7.3 the species found in the solution have $\varepsilon_{394}=104$ and $\varepsilon_{575}=133$ M^{-1} cm^{-1} ($M=mol\,dm^{-3}$) as reported for $[Cr^{III}(OH)(TOH)]^-$.[11] A stock solution of periodate was made up by weight and wrapped with Al foil to avoid photochemical decomposition.[13] Sodium dihydrogenphosphate, sodium hydroxide, and sodium nitrate solutions were made up by weight. Buffer solutions were made up from sodium dihydrogenphosphate–sodium hydroxide mixtures.

Kinetic Measurements. A Unicam SP8000 spectrophotometer, equipped with a thermostated cell holder, was used to monitor the reaction. The reactants in buffer solutions in the two compartments of an intended flask, were thermostated for about 20 minutes. These were thoroughly mixed and quickly transferred to an absorption cell. The formation of the chromium(VI) was followed at a wavelength in the 350—372 nm range where the absorption is maximal at the pH of the reaction. Pseudo-first order conditions were maintained in all runs by using a large excess of periodate concentrations (more than 10-fold) over those of $[Cr^{III}(H_2O)(TOH)]$. The pH of the reaction was measured on a Radiometer digital pH meter model PHM62. The ionic strength was maintained constant by using the appropriate amounts of sodium nitrate solution.

Results and Discussion

The stoichiometry of the $[Cr^{III}(H_2O)(TOH)]$-IO_4^- reaction can be represented by Eq. 1

$$2\,Cr^{III}+3\,I^{VII}\rightarrow 2\,Cr^{VI}+3\,IO_3^- \qquad (1)$$

where Cr^{III} and I^{VII} represent total chromium(III) and periodate, respectively. The concentration ratio of IO_4^- initially present to Cr^{VI} produced was found to be 1.50±0.04. The stoichiometry is also consistent with the observation that IO_3^- does not oxidize the chromium(III) complex over the pH range where the kinetics was investigated.

At all the chromium(III) complex concentrations used, in presence of vast excess of periodate, plots of $\ln(A_\infty-A_t)$ vs. time, where A_∞ and A_t are the absorbances at infinity and time *t*, respectively, were linear up to 85% of the reaction. The pseudo-first order rate con-

Table 1. Dependence of the $Cr^{III}(H_2O)(TOH)/IO_4^-$ Reaction Rate on $[Cr^{III}(H_2O)(TOH)]$, $[IO_4^-]$ at pH=7.30 and I=0.5 M,[a] at Different Temperatures

T	$10^2[IO_4^-]$	10^4k_{obs}
°C	M	s^{-1}
20	0.2	8.05±0.12
20	0.3	10.00±0.20
20	0.5	11.60±0.25
20	1.0	12.80±0.31
20	2.0	13.90±0.40
25	0.5	20.80±0.60
25	1.0	24.20±0.70
25	2.0	26.30±0.83
25	2.0	26.40±0.75[b]
25	2.0	26.25±0.80[c]
25	2.0	26.37±0.77[d]
25	3.0	27.02±0.79
25	4.0	27.39±0.85
25	5.0	27.77±0.80
30	0.2	20.80±0.64
30	0.3	25.00±0.81
30	0.5	29.40±0.90
30	1.0	36.60±1.20
30	2.0	40.50±1.34
35	0.5	42.60±1.28
35	1.0	52.60±1.40
35	2.0	60.61±1.43
35	3.0	65.32±1.50
35	5.0	66.70±1.49

a) Unless otherwise stated $[Cr^{III}(H_2O)(TOH)]=1.0\times10^{-4}$ M. For b), c), and d), $[Cr^{III}(H_2O)(TOH)]$ was 2.0×10^{-5} M, 5×10^{-5} M, and 2.0×10^{-4} M respectively.

stant, k_{obs}, was calculated from the slopes of these plots by using a linear least-squares program.

The constancy of k_{obs}, over the complex concentration range $(5.0—20.0)\times10^{-4}$ M under the fixed experimental conditions, shown in Table 1, is in agreement with a first-order dependence on its concentration.

The variation of k_{obs} with periodate concentration, Table 1, exhibits rate saturation at high periodate. Plots of $1/k_{obs}$ versus $1/[IO_4^-]$ were found to be linear with a definite intercept as shown in Fig. 1. The dependence of k_{obs} on periodate concentration is thus described by

$$k_{obs} = \frac{a[IO_4^-]}{1+b[IO_4^-]} \tag{2}$$

or

$$1/k_{obs} = \frac{1}{a[IO_4^-]} + \frac{b}{a}. \tag{3}$$

The values of a and b were obtained from the slope and the intercept as (1.52 ± 0.6) M^{-1} s^{-1} and (529 ± 15) M^{-1}, respectively at 25 °C and pH=7.30.

The effect of hydrogen-ion concentration on the reaction rate was investigated over the pH range 6.10—7.30. Table 2 shows that the rate of reaction increases with increasing pH value.

Table 2. Effect of pH on k_{obs} (s^{-1}) at $[Cr^{III}(H_2O)(TOH)]=1.0\times10^{-4}$ M, I=0.5 M, and T=25 °C

$10^2[IO_4^-]$	$10^4k_{obs}/s^{-1}$			
M	pH=7.30	pH=6.91	pH=6.56	pH=6.10
0.5	20.80±0.60	19.23±0.50	16.95±0.31	12.61±0.60
1.0	24.20±0.70	22.98±0.61	21.74±0.42	17.40±0.56
2.0	26.30±0.83	25.77±0.55	24.39±0.52	21.73±0.47
3.0	27.02±0.77	26.81±0.66	25.64±0.60	24.11±0.63
5.0	27.77±0.80	27.25±0.75	26.67±0.81	25.60±0.71

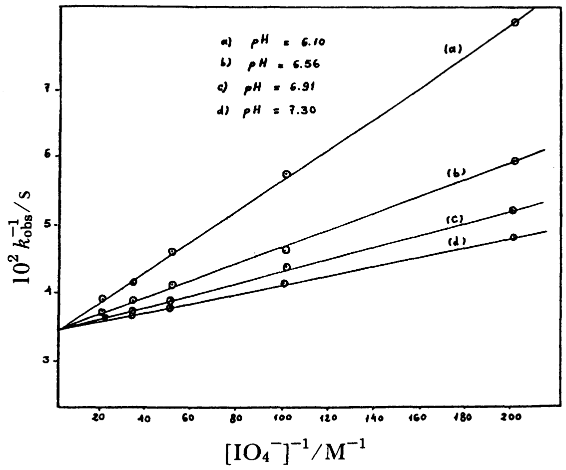

Fig. 1. Plots of k_{obs}^{-1} against $[IO_4^-]^{-1}$.

Bustin and Earley[14)] reported that $[Cr^{III}(H_2O)(TOH)]$ undergoes the following equilibria

$$[Cr^{III}(H_2O)(TOH)] \rightleftarrows [Cr^{III}(OH)(TOH)]^- + H^+;\ K_1 \tag{4}$$

$$[Cr^{III}(OH)(TOH)]^- \rightleftarrows [Cr^{III}(OH)(TO)]^{2-} + H^+;\ K_2 \tag{5}$$

with K_1 and K_2 having values of 3.63×10^{-7} M and 1.58×10^{-10} M, respectively at 25 °C and I=0.1 M. It is clear from the value of K_2 that $[Cr^{III}(OH)(TO)]^{2-}$ was not present at the employed pH values at the present study. The species present at low pH has the ligand bound in a quinquedentate manner, with the 2-hydroxyethyl group uncoordinated.[14)] The absence of an acid dissociation constant at pK_a ca. 3 precludes the presence of any uncomplexed-COO^- groups.[14)]

From the reported equilibrium constants of aqueous periodate solutions, it may be concluded that, over the H^+ range used in this study, the periodate species likely to be present are IO_4^-, $H_4IO_6^-$, and $H_3IO_6^{2-}$[15)] which are in the equilibria

$$H_4IO_6^- \rightleftarrows H_3IO_6^{2-} + H^+;\ K_3 = 5\times10^{-6} \tag{6}$$

$$H_4IO_6^- \rightleftarrows IO_4^- + 2H_2O;\ K_4 = 40. \tag{7}$$

It is clear from the value of K_4 that IO_4^- is not predominant species (I^{VII} will be used to represent $H_4IO_6^-$ and $H_3IO_6^-$).

The experimental rate equation suggests that a fast equilibrium step precedes the slow intramolecular electron transfer step. A possible mechanism is described by Eqs. 8—12.

$$[\mathrm{Cr^{III}(H_2O)(TOH)}] \rightleftarrows [\mathrm{Cr^{III}(OH)(TOH)}]^- + \mathrm{H^+};\ K_5 \quad (8)$$

$$[\mathrm{Cr^{III}(OH)(TOH)}]^- + \mathrm{I^{VII}} \rightleftarrows [\mathrm{(TOH)Cr^{III}(OH)\text{-}I^{VII}}]^-;\ K_6 \quad (9)$$

$$[\mathrm{(TOH)Cr^{III}(OH)\text{-}I^{VII}}]^- \xrightarrow{k_2} \mathrm{Cr^V} + \mathrm{IO_3}^- + \mathrm{TOH^{3-}} \quad (10)$$

$$\mathrm{Cr^V} + \mathrm{I^{VII}} \xrightarrow{\text{fast}} \mathrm{CrO_4}^{2-} + \mathrm{I^{VI}} \quad (11)$$

$$2\,\mathrm{I^{VI}} \xrightarrow{\text{fast}} \mathrm{I^{VII}} + \mathrm{IO_3}^- \quad (12)$$

From the above mechanism, rate of the reaction is given by

$$\begin{aligned}\text{rate} &= k_2[\mathrm{(TOH)Cr^{III}(OH)\text{-}I^{VII}}] \\ &= k_2K_6[\mathrm{Cr^{III}(OH)(TOH)^-}][\mathrm{I^{VII}}]. \quad (13)\end{aligned}$$

If $[\mathrm{Cr^{III}}]_\mathrm{T}$ represent the total concentrations of $\mathrm{Cr^{III}}$ species, then

$$\begin{aligned}[\mathrm{Cr^{III}}]_\mathrm{T} &= [\mathrm{Cr^{III}(OH)(TOH)^-}][\mathrm{H^+}]/K_5 \\ &+ [\mathrm{Cr^{III}(OH)(TOH)^-}] + K_6[\mathrm{Cr^{III}(OH)(TOH)^-}][\mathrm{I^{VII}}]. \quad (14)\end{aligned}$$

Substitution for $[\mathrm{Cr^{III}(OH)(TOH)^-}]$ from Eq. 14 into Eq. 13, gives

$$\text{rate} = k_2K_6[\mathrm{Cr^{III}}]_\mathrm{T}[\mathrm{I^{VII}}]_\mathrm{T}/1 + ([\mathrm{H^+}]/K_5) + K_6[\mathrm{I^{VII}}]_\mathrm{T} \quad (15)$$

and

$$k_\mathrm{obs} = k_2K_6[\mathrm{I^{VII}}]_\mathrm{T}/1 + ([\mathrm{H^+}]/K_5) + K_6[\mathrm{I^{VII}}]_\mathrm{T} \quad (16)$$

which on rearrangement, gives

$$1/k_\mathrm{obs} = K_5 + [\mathrm{H^+}]/k_2K_5K_6[\mathrm{I^{VII}}]_\mathrm{T} + 1/k_2. \quad (17)$$

At constant $[\mathrm{H^+}]$ Eq. 18 follows, in which A is a constant

$$1/k_\mathrm{obs} = A/k_2K_5K_6[\mathrm{I^{VII}}]_\mathrm{T} + 1/k_2 \quad (18)$$

which is identical to the experimental results shown in Eq. 3, where $a=k_2K_5K_6/A$ and $b=K_5K_6/A$.

Values of k_2 and K_6, at the temperature used, calculated from these relationships, by substitution $K_5=3.63\times10^{-7}$ M, are listed in Table 3. The activation parameters obtained from a least-squares' fit to the transition state theory equation are $\Delta H^{\ddagger}_{2}=76.0\pm2.1$ kJ mol^{-1} and $\Delta S^{\ddagger}_{2}=-38.7\pm7.1$ J K^{-1} mol^{-1}. The enthalpy of the pre-equilibrium reaction $\Delta H^{\circ}_{6}=-32.1\pm1.7$ kJ mol^{-1} is obtained from the temperature variation of K_6. Negative ΔS^{*} for the redox reactions between reactants with charges of the same sign were claimed to be largely the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated water molecules.[16] Value of $\Delta H^{\ddagger}_{6}$ indicates that the formation of the precursor complex $[\mathrm{(TOH)Cr^{III}(OH)\text{-}I^{VII}}]^-$, is an exothermic process as found in the reaction between $[\mathrm{Co^{II}(edta)^{2-}}]$ and $\mathrm{IO_4}^-$.[3] The intramolecular electron transfer step, is endothermic as indicated by the value of $\Delta H^{\ddagger}_{2}$.

Table 3. Values of k_2 and K_6 at Different Temperatures

T/°C	10^3k_2/s^{-1}	K_6/M^{-1}
20	1.50	751
25	2.95	596
30	4.31	503
35	7.30	414

The contributions of $\Delta H^{*}$and ΔS^{*} to the rate constant seem to compensate each other. This fact suggests that the factors controlling ΔH^{*} must be closely related to those controlling ΔS^{*}. Therefore, the solvation state of the encounter complex would be important in determining ΔH^{*}.[16] Thus, the relatively small enthalpy of activation, $\Delta H^{\ddagger}_{2}$, can be explained in terms of the formation of more solvated complex $[\mathrm{(TOH)\text{-}Cr^{III}(OH)\text{-}\ I^{VII}}]^-$.[17]

From Eq. 17 and Fig. 1, it follows that slopes of the plots can be represented by Eq. 19.

$$\text{slope} = [\mathrm{H^+}]/k_2K_5K_6 + 1/k_2K_6 \quad (19)$$

It is obvious, from Eq. 19 that the slope is dependent on $[\mathrm{H^+}]$. This plot is shown in Fig. 2 which indicates the validity of our proposed mechanism. Value of K_5 was calculated from Fig. 2, to be 2.70×10^{-7} M. This value is in good agreement with the reported[14] value of $K_5=3.63\times10^{-7}$ M at 25 °C. The equilibrium constant K_6 obtained from Eq. 19 and Fig. 2 is 571 M^{-1} which is in a good agreement ($K_6=596$ M^{-1}) with that obtained from Eq. 18 and Fig. 1 at 25 °C.

An innersphere mechanism is proposed for the oxidation of $[\mathrm{Cr^{III}(H_2O)(TOH)}]^-$ by $\mathrm{IO_4}^-$ in which the $[\mathrm{Cr^{III}(OH)(TOH)}]^-$ is bridged to $\mathrm{IO_4}^-$ through the hydroxo ligand because hydroxide on $[\mathrm{Cr^{III}(OH)\text{-}(TOH)}]^-$ is a better bridging ligand than $\mathrm{H_2O}$ on $[\mathrm{Cr^{III}(H_2O)(TOH)}]$. The assignment of an innersphere mechanism through the hydroxo bridge for this reaction seems to be supported by the following reasons: (i) Periodate ion is capable of acting as a ligand as evidenced from its coordination to copper(III)[18] and nickel(IV).[19] (ii) The hydroxo ligand is a firm ligand bridge. (iii) No reaction was observed at pH below 6.0 where the hydroxo species is not present. (iv) The inverse dependence of $[\mathrm{H^+}]$ is usually ascribed to oxidation of the hydroxy species offering a very effective OH bridge in an innersphere process.[20]

The oxidation of $[\mathrm{Cr^{III}(H_2O)(TOH)}]$ by $\mathrm{IO_4}^-$ may proceed via one- or two-electron transfer giving $\mathrm{Cr^{IV}}$ or

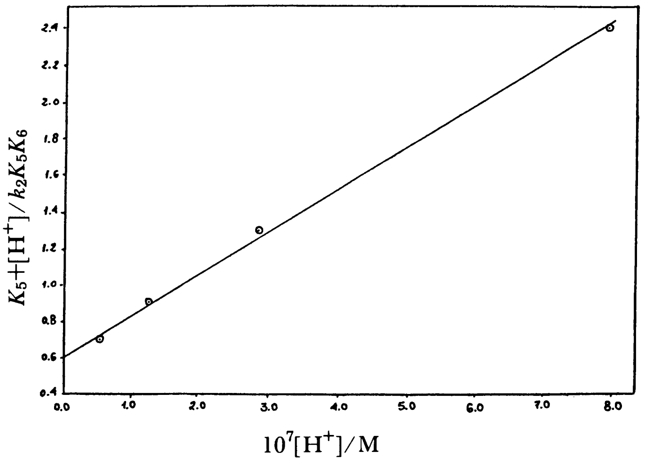

Fig. 2. Plots of $K_5+[\mathrm{H^+}]/k_2K_5K_6$ vs. $[\mathrm{H^+}]$.

Cr^{V}, respectively in the rate determining step. These may then followed by a fast step leading to Cr^{VI}. The fact that acrylonitrile was not polymerized seems to support two-electron transfer process.

In comparison with oxidation of $[Cr^{III}(edta)(H_2O)]$,[7] under the same conditions, the both hydroxy complexes, $[Cr^{III}(edta)(OH)]^{2-}$ and $[Cr^{III}(OH)(TOH)]^{-}$, are significantly more reactive than their conjugate acids. Value of k_2K_6 (k_2 is the intramolecular transfer rate constant and K_6 is the pre-equilibrium formation constant), for the oxidation of $[Cr^{III}(H_2O)(TOH)]$, is equal to 1.74 at 25 °C. This value is very close to the value of $k^{et}K_4$ (1.81 ± 0.18) for the oxidation of $[Cr^{III}$-$(edta)(H_2O)]$, where $k^{et}K_4$ corresponds to k_2K_6. It would be more informative to compare the intramolecular electron transfer rate constants. However, this is not possible because the value of k^{et} for the edta complex is not known.

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