Kinetics and mechanism of oxidation of two new chromium(III) complexes by hydrogen peroxide

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The kinetics and mechanism of oxidation of $[Cr(1,3\text{-diaminopropane})_2(NCS)_2]NCS.4H_2O$ and $[CrLCl_2]Cl.2H_2O$ (L = Schiff base, $C_{17}H_{24}N_4S_2$ derived from condensation of N,N-bis-(2-aminoethyl)-1,3-propanediamine and thiophen-2-aldehyde) by hydrogen peroxide have been investigated spectrophotometrically at 30°C. The reactions proceed through a rapid pre-equilibrium formation of a peroxide adduct which dissociates through cleavage of oxygen-hydrogen, metal-chlorine (rate-determining) and oxygen-oxygen bonds to give a dioxo Cr(IV) product which on further oxidation by a second H_2O_2 molecule gives Cr(VI) oxo-product. Different kinetic parameters of the reactions have been calculated and the general mechanism of the reactions has been postulated.

Peroxo complexes have received wide spread attention in synthetic areas[1-4] during past few decades. But very little information is available[5] on the kinetic aspects of hydrogen peroxide reaction of transition metal complexes. Studies on the comparison of the reactivity of peroxo derivatives of d^0 transition metal ions with that of free hydrogen peroxide have appeared in some reports[6-8]. Ranganathan et al.[9] have studied the kinetics of hydrogen peroxide reactions of diperoxo aqua (ethylenediamine) chromium (IV), $Cr(O_2)_2(en)(H_2O)$ and diperoxo (diethylene-triamine) chromium(IV), $Cr(O_2)_2(dien)$ and the evidence of formation of an oxodiperoxo chromium(VI) intermediate has been established.

We reported earlier[5] the kinetics of hydrogen peroxide reaction of some halo Schiff base Cr(III) complexes. The present study is an extension of the earlier one and we report herein the kinetics and mechanism of oxidation of two new chromium(III) complexes, $[Cr(1,3\text{-diaminopropane})_2(NCS)_2]NCS. 4H_2O$ and $[Cr(C_{17}H_{24}N_4S_2)Cl_2]Cl.H_2O$ ($C_{17}H_{24}N_4S_2$ = Schiff base) by hydrogen peroxide.

Materials and Methods

Hydrogen peroxide, sodium hydroxide, and perchloric acid were used as supplied by Merck and BDH.

Kinetic studies

The chromium(III) complexes, $[Cr(1,3\text{-diamino-propane})_2(NCS)_2]NCS\cdot 4H_2O$ and $[CrLCl_2][Cl\cdot H_2O$

(L = Schiff base, $C_{17}H_{24}N_4S_2$ derived from condensation of N,N-bis(2-aminoethyl)-1,3-propanediamine and thiophen-2-aldehyde) have been isolated by the procedures reported earlier[10,11] [Complex, $[Cr(1,3\text{-diaminopropane})_2(NCS)_2]NCS\cdot 4H_2O$: IR spectra: v_{sym} $(NH_2) = 3020$ $cm^{-1}(m)$, v_{asym} $(NH_2) = 3240$ $cm^{-1}(m)$ (ligand value 3295-3360 cm^{-1}), $v(C=S) = 1025$ $cm^{-1}(m)$, $v(Cr-N) = 520$ $cm^{-1}(m)$. Anal. Found: C, 24.1; H, 4.5; N,21.9; Calc. C, 24.2; H, 4.5; N, 22.0%. Complex, $[CrLCl_2]Cl\cdot H_2O$: IR spectra: $v(C=N) = 1600$ $cm^{-1}(s)$ (~ 30 cm^{-1} shift towards lower frequency compared to the ligand value), $v(Cr-N) = 510$ cm^{-1} (m), $v(Cr-S) = 365$ $cm^{-1}(w)$. Anal. Found: C, 38.7; H, 4.8; N, 10.5; Calc. C, 38.9; H, 4.9; and N = 10.7%].

Earlier some experiments were performed to find out λ_{max} for the complexes. The oxidation kinetics of these complexes were studied on an LKB Biochrom Ultrospec K 4053 UV-visible spectrophotometer at 30°C, [complex] ≈ 1 m mol dm^{-3}, $[H_2O_2] = 1.0\text{-}9.8$ mol dm^{-3} and $\lambda = 371$ and 404 nm.

For each kinetic measurement, about 2-3 mg of each of the complexes was dissolved in 5 cm^3 aqueous H_2O_2 solution, the clear solution was transferred quickly to a 2 cm^3 quartz cell and the molar absorbances were recorded at regular time intervals. Kinetic measurements were performed in the presence of $HClO_4$-NaOH buffer also in the pH range 2.15-10.15 at $[H_2O_2] = 5.0$ mol dm^{-3} and [complex] ≈ 1 m mol dm^{-3}. The absorbance data were used to find out the observed rate con-

Table 1—Pseudo-first order rate constants, k_{obs}, for the oxidation of [Cr(1,3-diaminopropane)₂(NCS)₂]⁺ and [CrLCl₂]⁺ (L= Schiff base, $C_{17}H_{24}N_4S_2$) by hydrogen peroxide at 30°C

[Cr(1,3-diaminopropane)₂(NCS)₂]⁺ $\lambda = 404$ nm		[CrLCl₂]⁺ $\lambda = 371$ nm	
H_2O_2 (mol dm⁻³)	$10^3 k_{obs}$ (s⁻¹)	H_2O_2 (mol dm⁻³)	$10^3 k_{obs}$ (s⁻¹)
0.5	1.61	0.5	1.54
1.0	2.53	1.0	2.41
2.5	3.33	2.5	3.24
5.0	3.96	5.0	3.83
7.5	4.38	7.5	3.84
9.8	4.45	9.8	3.99

Fig. 1—Dependence of observed rate constants, k_{obs} on H_2O_2 concentration for the oxidation reactions of [Cr(1,3-diaminopropane)₂(NCS)₂]₊ (●) and [CrLCl₂]⁺ (L=$C_{17}H_{24}N_4S_2$) (▲) by hydrogen peroxide at 30°C

stants from the pseudo-first order plots. The pH values of the buffer solutions were measured by a digital Jenway 3030 pH-meter.

Results and Discussion

Under the pseudo-first order conditions ([H₂O₂] ≫ [complex]), the observed rate constants, k_{obs}, for the oxidation have been calculated from the plots of $\ln(A_t - A_\infty)$ versus time (t) according to Eq. (1).

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - kt \qquad \dots (1)$$

where A_0 is the initial molar absorbance and A_t and A_∞ are those at time t and at the end of the reaction.

The observed rate constants (Table 1) increase nonlinearly with increase in [H₂O₂] (Fig. 1). Thus the present kinetic data are indicative of a reaction path that involves a rapid pre-equilibrium peroxide adduct formation (Eq. 2) prior to dissociation of the adduct. The complete dissociation of the adduct comprises of three elementary reactions, viz., (i) rate-determining liberation of two chloride ligands (Eq. 3), (ii) release of two protons (Eq. 4) from O−H bonds and (iii) cleavage of oxygen-oxygen bond coupled with oxidation of the metal from oxidation state III to IV (Eq. 5) forming the dioxo Cr(IV) product. This oxo product is finally converted to Cr(VI) oxo-product through a fast step involving further attack with a second oxidant molecule (Eq. 6).

The oxidation process primary initiated by the rapid formation of an adduct with the oxidant molecule (H₂O₂) is virtually controlled by the cleavage of M−Cl bonds. The cleavage of M−Cl bonds facilitates the oxidation of the metal (Eq. 5). The rate-controlling nature of cleavage of M−Cl bond is understood by the fact that the release of two chloride ligands from the 8-coordinated ad-

duct renders O−H hydrogens acidic and are easily abstracted. The subsequent breaking of oxygen-oxygen bond and the oxidation of the metal are also very much related to the release of the coordinated chlorides. The overall reaction is outlined in Scheme 1 (applicable for [CrLCl₂]⁺, as an example (L= quadridentate Schiff base, $C_{17}H_{24}N_4S_2$).

$$Cr^{III}LCl_2^+ + H_2O_2 \xrightleftharpoons{K_{aq}} Cr^{III}LCl_2 \cdot H_2O_2^+ \qquad \dots (2)$$

(Complex)   (Adduct)

$$Cr^{III}LCl_2 \cdot H_2O_2^+ \xrightarrow[\text{slow}]{k} Cr^{III}L \cdot H_2O_2^{3+} + 2Cl^- \dots (3)$$

$$Cr^{III}L \cdot H_2O_2^{3+} \xrightarrow{\text{fast}} Cr^{III}LO_2^+ + 2H^+ \qquad \dots (4)$$

$$Cr^{III}LO_2^+ \xrightarrow{\text{fast}} Cr^{IV}(O)_2L \qquad \dots (5)$$

$$Cr^{IV}(O)_2L + H_2O_2 \xrightarrow{\text{fast}} Cr^{VI}O_3 + L + H_2O \qquad \dots (6)$$

Scheme 1

The rate law for Scheme 1 is represented by Eq. (7).

$$-d[\text{Complex}]/dt = k_{obs}([\text{Complex}] + [\text{Adduct}])$$

$$= k[\text{Adduct}] \qquad \dots (7)$$

Equation (8) is obtained on rearranging Eq. (7).

$$k_{obs} = \frac{kK_{eq}[H_2O_2]}{1 + K_{eq}[H_2O_2]} \qquad \dots (8)$$
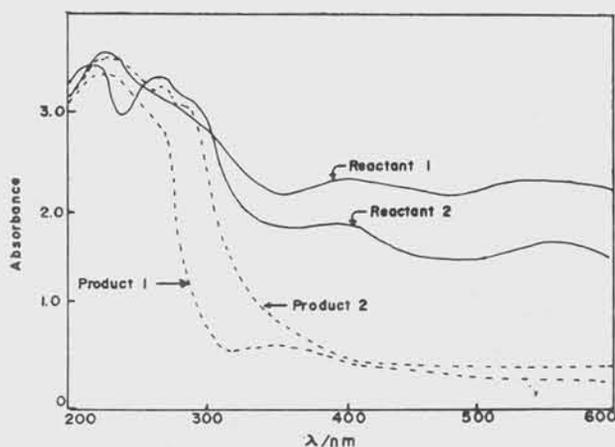
Fig. 2—Comparative UV-vis. spectra of thiocyanato and chloro Schiff base Cr(III) complexes and the corresponding H_2O_2 reaction products. Spectra marked as reactants 1 and 2 represent thiocyanato and chloro Schiff base complexes, respectively and those marked as products 1 and 2 represent H_2O_2 reaction products of thiocyanato and chloro Schiff base complexes, respectively

Table 2—Pseudo-first order rate constants, k_{obs} for the reactions of $[Cr(1,3\text{-diaminopropane})_2(NCS)_2]^+$ and $[CrLCl_2]^+$ (L=Schiff base, $C_{17}H_{24}N_4S_2$) by hydrogen peroxide at 30°C, $[H_2O_2] = 5.0$ mol dm^{-3} and at different pH

$[Cr(1,3\text{-diaminopropane})_2(NCS)_2]^+$		$[CrLCl_2]^+$	
pH	$10^3\,k_{obs}$ (s^{-1})	pH	$10^3\,k_{obs}$ (s^{-1})
2.14	3.75	2.14	4.82
4.11	3.62	4.11	4.37
6.15	2.92	6.15	4.18
8.00	3.28	8.00	4.44
10.15	3.47	10.15	4.55

k and K_{eq} can be calculated from the linear double reciprocal plot of $1/k_{obs}$ versus $1/[H_2O_2]$ (see Eq. 8) and the plot yielded K_{eq} values of 0.985 and 1.15 and k values of 4.81×10^{-3} and 4.26×10^{-3} s^{-1} respectively for the complexes with bidentate amine and quadridentate Schiff base.

The data (Table 1) reveal that pseudo-first order rate constants are larger for the complex with bidentate amine than those for the complex with the quadridentate Schiff base, thereby reflecting a comparative electronic effect of the coordinated ligands on the observed rates. The intermediate adduct, being a loosely bound 8-coordinated species, is very unstable. Similar type of peroxo adduct has been reported by Eldik et al.[12] in the oxidation kinetic study of Fe^{II} complexes by molecular oxygen. This adduct undergoes a subsequent dissociation leading to a Cr(IV) species through an elementary rate-determining step (Eq. 3) followed by two rapid reactions (Eqs 4 and 5) and finally leads to the formation of Cr(VI) (d^0) species (Eq. 6). This is evident from the gradual development of yellow colour in the reaction mixtures and the absence of d-d bands in the UV-vis spectra of the product solutions (Fig. 2) giving only charge transfer bands. The Cr(VI) oxo product was estimated quantitatively from bulk reactions (62 mg of thiocyanato complex or 84 mg of the Schiff base complex yielded ~ 15 mg of CrO_3). The free ligands in the product solutions were identified from IR spectra (as polystyrene film) viz., $\nu_{sym}(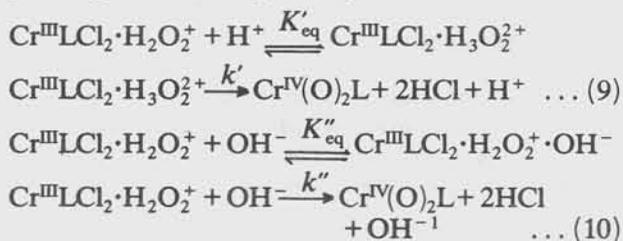NH_2)$ and $\nu_{sym}(NH)$ modes at 3295 cm^{-1} and 3350 cm^{-1} respectively for the bidentate diamine ligand and $\nu(C=N)$ mode at 1630 cm^{-1} for the Schiff base ligand were observed.

The formation and accumulation of the adduct is more favourable for complex with the Schiff base which is rationalised in terms of the higher value of K_{eq} and lower value of k compared to those of complex with bidentate amine. This is probably due to the preferential positioning of the peroxo moiety in the large cavity of the 12-membered metal-ligand ring of the Schiff base complex. The comparatively higher stability of the peroxo adduct with the Schiff base complex renders slower rate of dissociation to Cr(IV) dioxo product. Despite the larger steric hindrance of the Schiff base moiety compared to bidentate amine ligand the larger stability of the peroxo adduct of the Schiff base complex can be viewed due to comparatively greater coulombic attraction between the metal centre and the peroxo moiety, because in the case of bidentate amine complex, four amine N donors neutralise the charge on the metal centre to a greater extent than the neutralization caused by two imine N and two S donors of the quadridentate Schiff base.

The pH dependence of the observed rate constants is shown in Table 2. This can be explained in terms of acid and base-catalysed reactions[12] occurring in lower and higher pH ranges respectively. The significant increase of k_{obs} from 2.92×10^{-3} s^{-1} to 3.75×10^{-3}s^{-1} for thiocyanato complex and 4.18×10^{-3}s^{-1} to 4.82×10^{-3}s^{-1} for the Schiff base complex with the decrease in pH in the range 6.15-2.11 is attributed to the simultaneous or parallel acid-catalysed running concurrently with the peroxide oxidation process. But the increase in k_{obs} from 2.92×10^{-3}s^{-1} to 3.47×10^{-3}s^{-1} for the thiocyanato complex and 4.18×10^{-3}s^{-1} top 4.55×10^{-3}s^{-1} for the Schiff base complex beyond pH = 6.15 is probably due to the base-catalysed reactions occurring parallel

to the peroxide oxidation. The presence of buffer in the reaction systems seems to retard the peroxide oxidaton in the case of bidentate amine complex for reasons not clear, thereby giving lower k_{obs} values than is expected.

The acid and base-catalysed reactions at constant $[H_2O_2]$ and [complex] that occur concurrently with peroxide oxidation can be shown in Scheme 2 (Eqs 9 and 10) involving protonation and hydroxylation of the hydrogen peroxide adduct in the lower pH range (<6.15) and higher pH range (>7.0), respectively.

$$Cr^{III}LCl_2 \cdot H_2O_2^+ + H^+ \underset{}{\overset{K'_{eq}}{\rightleftharpoons}} Cr^{III}LCl_2 \cdot H_3O_2^{2+}$$

$$Cr^{III}LCl_2 \cdot H_3O_2^{2+} \overset{k'}{\longrightarrow} Cr^{IV}(O)_2L + 2HCl + H^+ \quad \ldots (9)$$

$$Cr^{III}LCl_2 \cdot H_2O_2^+ + OH^- \underset{}{\overset{K''_{eq}}{\rightleftharpoons}} Cr^{III}LCl_2 \cdot H_2O_2^+ \cdot OH^-$$

$$Cr^{III}LCl_2 \cdot H_2O_2^+ + OH^- \overset{k''}{\longrightarrow} Cr^{IV}(O)_2L + 2HCl + OH^{-1} \quad \ldots (10)$$

Scheme 2

The rate laws for the pH-dependence (Eqs 11 and 12) are expressed taking Eqs 9 and 10 individually with Eqs 2-6.

$$k_{obs} = \left\{ \frac{k + k' \, K'_{eq} [H^+]}{1 + K'_{eq} [H^+]} \right\} K_{eq} [H_2O_2] \quad \ldots (11)$$

(at $pH < 6.15$)

$$k_{obs} = \left\{ \frac{k + k'' \, K''_{eq} [OH^-]}{1 + K''_{eq} [OH^-]} \right\} K_{eq} [H_2O_2] \quad \ldots (12)$$

(at $pH > 7.00$)

Under the present situation (i.e., at low $[H^+]$ or $[OH^-]$), $1 + K'_{eq}[H^+] \approx 1$ and $1 + K''_{eq}[OH^-] \approx 1$. Therefore, Eqs 11 and 12 reduce to Eqs 13 and 14, respectively.

$$k_{obs} = \{ k + k' \, K'_{eq} [H^+] \} K_{eq} [H_2O_2] \quad \ldots (13)$$

$$k_{obs} = \{ k + k'' \, K''_{eq} [OH^-] \} K_{eq} [H_2O_2] \quad \ldots (14)$$

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