Kinetic Studies on the Reaction of Ethylenediaminetetraacetatochromium(III) Complex with Hydrogen Peroxide

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Abstract

The rate of reaction of $[Cr(III)Y]_{aq}$ (Y is EDTA anion) with hydrogen peroxide was studied in aqueous nitrate media $[\mu = 0.10$ M $(KNO_3)]$ at various temperatures. The general rate equation,

$$\text{Rate} = \frac{k_1 + k_2 K_1 [H^+]^{-1}}{1 + K_1 [H^+]^{-1}} [Cr(III)Y]_{aq}[H_2O_2]$$

holds over the pH range 5–9. The decomposition reaction of H_2O_2 is believed to proceed *via* two pathways where both the aquo and hydroxo-quinquedentate EDTA complexes are acting as the catalyst centres. Substitution-controlled mechanisms are suggested and the values of the second-order rate constants k_1 and k_2 were found to be 1.75×10^{-2} M^{-1} s^{-1} and 0.174 M^{-1} s^{-1} at 303 K respectively, where k_1 is the rate constant for the aquo species and k_2 is that for the hydroxo complex. The respective activation enthalpies ($\Delta H_1^* = 58.9$ and $\Delta H_2^* = 66.5$ KJ mol^{-1}) and activation entropies ($\Delta S_1^* = -85$ and $\Delta S_2^* = -40$ J mol^{-1} deg^{-1}) were calculated from a least-squares fit to the Eyring plot. The ionisation constant pK_1, was inferred from the kinetic data at 303 K to be 7.22. Beyond pH 9, the reaction is markedly retarded and ceases completely at pH $\geqslant 11$. This inhibition was attributed in part to the continuous loss of the catalyst as a result of the simultaneous oxidation of Cr(III) to Cr(VI).

Introduction

The disproportionation of hydrogen peroxide is catalysed by several aquo metal ions and their complexes. The catalytic activity of these complexes has been correlated in part to the electronic structure of the metal ion and its ability to form two or more different oxidation states of reasonable stability [1, 2], and partly to the structure of the metal complex, which in turn is related to the availability and lability of free coordination sites within the coordination sphere [3, 4].

Of particular interest are the models proposed to study the mechanism of formation, decomposition and substrate reactions of biologically important peroxy metal chelates such as catalase, peroxidase and vitamin B_{12}. Among these species are the aminopolycarboxylate complexes of iron [5–8], vanadium [9–13], cobalt [14, 15] and manganese [16]. Almost in every case reported there is a general agreement that decomposition proceeds through an intermediate involving hydrogen peroxide in the inner-sphere [17, 18] and the reaction is substitution controlled [8]. A unique example of the assessment of the role played by the metal lability is that involving chromium centers.

Earlier studies on hydrogen peroxide decomposition in the presence of chromium species were limited to reactions involving the hexacyanochromium(II) complex [19]. The results were interpreted in terms of both outer- and inner-sphere mechanisms when the oxidants are the neutral H_2O_2 or hydroperoxyl ion repectively. In the present work we extend the discussion to the relatively inert chromium(III) complex with EDTA.

Oxidation Products and Stoichiometry

Preliminary studies of the reaction of $H[CrY(H_2O)]$ (here and elsewhere Y represents the tetranegative EDTA anion) with H_2O_2 indicated that the type of product is a function of the pH of the medium. This was assessed by monitoring the absorbance changes with time, under different experimental conditions.

In the absence of hydrogen peroxide and in acidic medium (pH < 5), the spectrum of the chromium(III)–EDTA complex displays bands at 390 nm and 540 nm. The latter band shifts to 590 nm upon increasing the pH to a value > 8.0. The molar absorptivity for solutions buffered at pH 9.8 were found to be 61 and 87 dm^3 mol^{-1} cm^{-1} at the two wavelengths, respectively. In strongly alkaline solutions (pH > 9.0) and in the presence of large excess of hydrogen peroxide, the blue colour characteristic

for the $[CrY(OH)]^{2-}$ species fades slowly and the solution turns yellow, with the development of a new intense band at 372 nm at the expense of the other two bands at 390 and 590 nm, as shown in Fig. 1. This colour change is associated with the oxidation of the chromium(III) complex to chromate anion (λ_{max} 372; ϵ_{max} 8.2×10^3 dm^3 mol^{-1} cm^{-1}). The amount of formed chromate at any time t, was calculated using the relationship,

$$[CrO_4^{2-}]_t = (A_t - A_i)/(\epsilon_{CrO_4} - \epsilon_{Cr(III)}) \qquad (1)$$

where A_t and A_i are the observed and initial absorbances, respectively.

Measurements of the consumption ratio R_∞ (= $\Delta[H_2O_2]/\Delta[CrO_4]$) for the oxidation reaction of Cr(III) → Cr(VI) were attempted at two different stages. Solutions obtained at the end of a typical kinetic run were analysed both iodometrically for

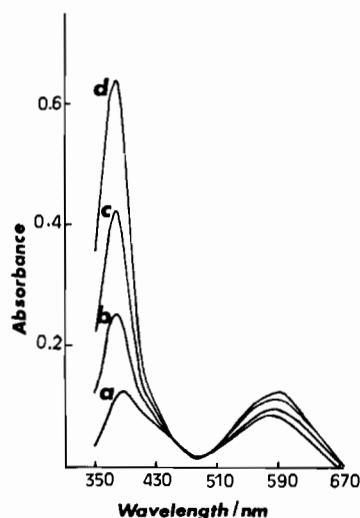Fig. 1. Change in absorbance as a function of time in the reaction between $[Cr(III)Y]_{aq}$ (1.549 mmol dm^{-3}) and H_2O_2 (50.0 mmol dm^{-3}) at pH 9.80. a) after 1 min; b) after 3 min; c) after 6 min; and d) after 10 min.

the total contents of residual H_2O_2 and formed chromate and spectrophotometrically for the final chromate concentration using the above relationship. Alternatively, the values of R were obtained by quenching the reaction solutions with H_2SO_4/KI mixtures after a fixed time (60 min) then analysing for the chromium and peroxide contents. The results obtained are given in Table I. Obviously, the catalytic decomposition of hydrogen peroxide is too rapid to allow for a reliable estimate of the stoichiometry of the peroxidatic reaction. It is also clear that the ratio of the catalytic/peroxidatic processes is influenced by both the relative initial concentrations of the reactants and the pH of the medium. Thus at pH 7.4, more than 96% of the total chromium(III)–EDTA complex is retained within the first two half-lives of the disproportionation reaction. Measurements obtained at pH < 7.0 showed that the reaction is entirely catalytic.

Results and Discussion

Preliminary experiments in which the ratios of $[EDTA]/[Cr(III)Y]_{aq}$ were 0–3 showed that the rate of decomposition of the peroxide is insensitive to the amount of free EDTA present in solution. However, in all experiments a small excess of Na_2-H_2Y was added to the reaction solution for its dual action as a buffering medium and to minimise the concentration—if any—of the free chromium(III) contents below the solubility of the metal hydroxide.

Pseudo first-order conditions were maintained in all runs by using a large excess of hydrogen peroxide concentration over that of the $[Cr(III)Y]_{aq}$ complex. Plots of the logarithmic value of the residual concentration of H_2O_2 vs. time were linear up to 75% of the decomposition reaction. Up to this stage, the ratio of the residual peroxide/$[Cr(III)Y]_{aq}$ was greater than 8, as calculated from the initial reaction

TABLE I. Dependence of the Consumption Ratio, R, on the Initial Conditions.

$[H_2O_2]_i$ (mmol dm^{-3})	$[Cr(III)Y]_i$ (mmol dm^{-3})	pH	$[Cr(VI)]_{60}$ (mmol dm^{-3})	$[Cr(VI)]_\infty$[a] (mmol dm^{-3})	R_{60}	R_∞
2.3	1.549	9.80		0.096		4.05
11.9	1.549	9.80	0.110		26.7	
45.6	1.549	9.80	0.315		52.0	
30.0	1.549	9.80	0.206	0.465		51.60
30.0	1.549	9.50	0.131	0.244		117.60
30.0	1.549	8.85	0.041	0.161		176.48
50.0	1.549	7.40		0.058		
50.0	1.549	9.80		0.760		
50.0	1.068	9.80		0.547		
50.0	0.641	9.80		0.334		

[a]Values measured after 24 h.

conditions given in Table II. The pseudo first-order rate constants obtained from the slopes of these plots using a linear least squares programme are collected in Table II. At fixed conditions of hydrogen ion and peroxide concentrations the values of k_{obs} were an increasing linear function of the chromium complex concentration as is illustrated in Fig. 2. It follows,

$$\text{Rate} = -d[H_2O_2]/dt = k_{obs}[H_2O_2]$$
$$= k[Cr(III)Y]_{aq}[H_2O_2] \qquad (2)$$

where,

$$[Cr(III)Y]_{aq} = [Cr(HY)(H_2O)] + [CrY(H_2O)]^-$$
$$+ [CrY(OH)]^{2-} + [CrY(OH)_2]^{3-} \qquad (3)$$

TABLE II. Observed Rate Constants for the Reaction of Hydrogen Peroxide with $[Cr(III)Y]_{aq}$[a]; $[EDTA]_f$[b] = 3 mmol dm^{-3}; H_2O_{2i} = 0.05 mol dm^{-3}; μ = 0.10 mol dm^{-3} (KNO$_3$).

$-\log[H^+]$	$[Cr(III)Y]_{aq}$ (mmol dm^{-3})	Temp. (°C)	$k_{obs}/10^{-5}$ (s^{-1})
5.24	1.549	30	1.56
6.13	1.549	30	3.45
6.13	1.549	38	8.83
6.14	1.549	45	15.35
6.57	1.549	30	7.17
6.55	1.068	30	5.00
6.57	0.641	30	2.83
6.56	1.549	38	15.35
6.56	1.549	45	24.18
6.71	1.549	30	8.83
6.95	1.549	30	13.05
6.93	1.549	38	23.80
6.93	1.549	45	38.38
7.49	1.549	30	18.16
8.09	1.549	30	21.51
8.69	0.668	30	11.47
8.69	1.068	30	17.66
8.68	1.549	30	24.25
8.68	2.030	30	30.79
9.08	0.641	30	11.62
9.08	1.068	30	16.47
9.08	1.549	30	25.20
9.09	2.030	30	31.43
9.37	0.641	30	8.92
9.39	1.068	30	14.10
9.38	1.549	30	21.39
9.79	0.668	30	6.15
9.79	1.068	30	8.27
9.78	1.549	30	12.49
9.77	2.057	30	16.90
10.29	0.641	30	1.96
10.29	1.068	30	2.90
10.28	1.549	30	5.10
10.28	2.030	30	6.86

[a]The total concentration of chromium(III)–EDTA in all forms.   [b]Free EDTA.

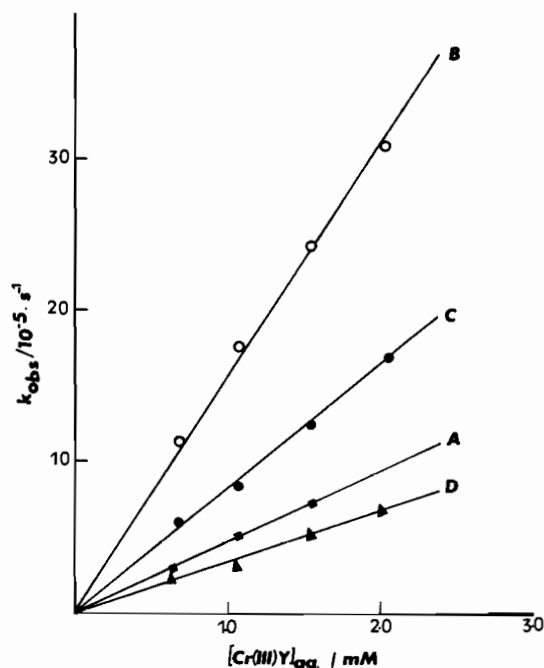Fig. 2. Plots of the observed first-order rate constants (k_{obs}) *vs.* $[Cr(III)Y]_{aq}$ concentration at the pH values, A) 6.68; B) 8.80; C) 9.90 and D) 10.40. (μ = 0.10 mol dm^{-3} (KNO$_3$); temp. = 303 K and $[H_2O_2]$ = 50.0 mmol dm^{-3}).
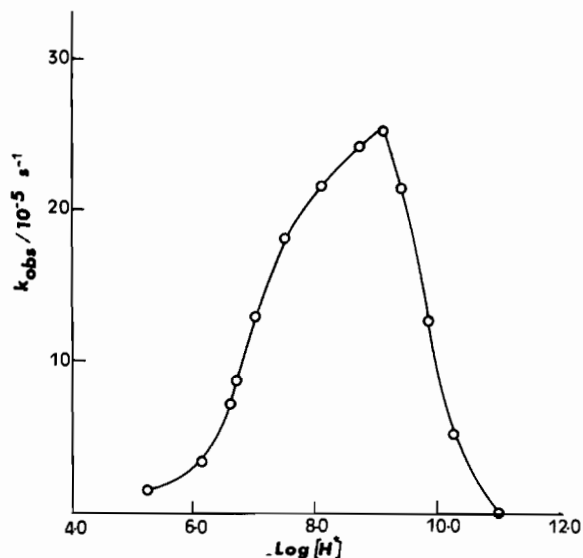

Fig. 3. The variation of k_{obs} with $-\log[H^+]$ for the reaction of H$_2$O$_2$ with $[Cr(III)Y]_{aq}$. (μ = 0.10 mol dm^{-3} (KNO$_3$); temp. = 303 K and $[Cr(III)Y]_{aq}$ = 1.549 mmol dm^{-3}).
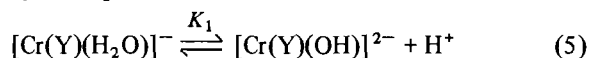
The pH dependency is rather complex. Figure 3 represents a plot of k_{obs} as a function of $-\log[H^+]$. In the pH region 5.3–9.2, the k_{obs}–pH relationship resembles the profile of an acid-base titration curve. This strongly suggests that one of the reactants is

involved in an acid—base equilibrium in this pH range. Beyond pH 9.2, the reaction is sharply retarded with increasing the pH of the medium, and it ceases completely at pH 11.
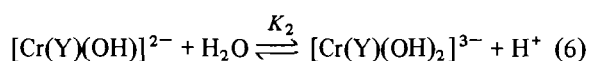
Earlier studies on chromium-EDTA system revealed that EDTA binds chromium(III) ions using both nitrilo and three carboxylic groups, while the remaining coordination site is occupied by a water molecule [20]. The quiquedentate nature of EDTA was also confirmed by IR spectroscopy [21] which showed that in the species [Cr(HY)(H$_2$O)] the proton is associated with the free carboxylic group. Addition of one equivalent of alkali results in the dissociation of this proton as is shown in eqn. 4,

$$[Cr(HY)(H_2O)] \rightleftharpoons [Cr(Y)(H_2O)]^- + H^+ \qquad (4)$$

and the pK_a value was determined to be 3.10 [22]. Further addition of base leads to the formation of the mono- and dihydroxo complexes as represented by the equilibria,

$$[Cr(Y)(H_2O)]^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Cr(Y)(OH)]^{2-} + H^+ \qquad (5)$$

and

$$[Cr(Y)(OH)]^{2-} + H_2O \underset{}{\overset{K_2}{\rightleftharpoons}} [Cr(Y)(OH)_2]^{3-} + H^+ \quad (6)$$

with pK values 7.39 and 12.2 respectively [22, 23]. In the dihydroxo species, EDTA acts as a quadridentate ligand and the value of 12.2 is in fact, a multiparameter constant involving a water molecule substitution followed by proton dissociation [24]. In the pH region 5.3—11.0 the only species which are significantly present in solution are the aquo- and the monohydroxo complexes. This excludes the possibility of having a third inactive species responsible for the retardation observed beyond pH 9.2, and this catalytic inhibition is probably associated with changes in the reaction pathways.

Peroxidatic-Catalytic Decomposition in Alkaline Media

Although the overall dependency on [H$_2$O$_2$] and [Cr(III)Y]$_{aq}$ concentrations looks apparently simple, as indicated by the linear first order plots of the peroxide loss as well as the direct proportionality of the k_{obs} values on the initial contents of [Cr(III)Y]$_{aq}$ concentration (cf. Fig. 2C and D), this system at pH values greater than 8—9 proved however to be of an exceptional chemical complexity.

As it has been shown earlier, in alkaline media part of the chromium(III) contents is oxidised to chromate. The extent of this oxidation reaction is dependent on the relative initial reactant concentrations and the pH of the medium. Apart from the retardation of decomposition as a result of the continuous loss of the Cr(III) catalyst by time, the

chromate ion is self-acting as a catalyst for H$_2$O$_2$ disproportionation. Haggett et al. [25] showed that the rate of decomposition is accurately first-order in the chromate concentration, whereas the dependency on hydrogen peroxide passes through a maximum then showed a minimum value and began to increase once more with increasing the mol fraction of H$_2$O$_2$. They interpreted their observations in terms of a mechanism involving the formation of an active monoperoxo complex, inactive diperoxo complex and possibly at high mol fraction of H$_2$O$_2$, a triperoxo and/or tetraperoxo active intermediates are formed. Apparently, catalysis by chromate is much slower than that by [CrY(OH)]$^{2-}$ species, as indicated by the overall slowing in the rate of decomposition of hydrogen peroxide. Additional problems arise from the fact that chromate anion tends to associate with the monohydroxo-EDTA complex [26] thus competing with H$_2$O$_2$ and/or HOO$^-$ ion for the available site on the chromium coordination sphere.

Attempts to evaluate the kinetic parameters for the oxidation reaction of chromium(III) to chromium(VI) were unsuccessful. As shown in Fig. 4, plots of log(d[Cr(VI)]/dt) vs. log[Cr(III)]$_t$ in the presence of large excess of hydrogen peroxide
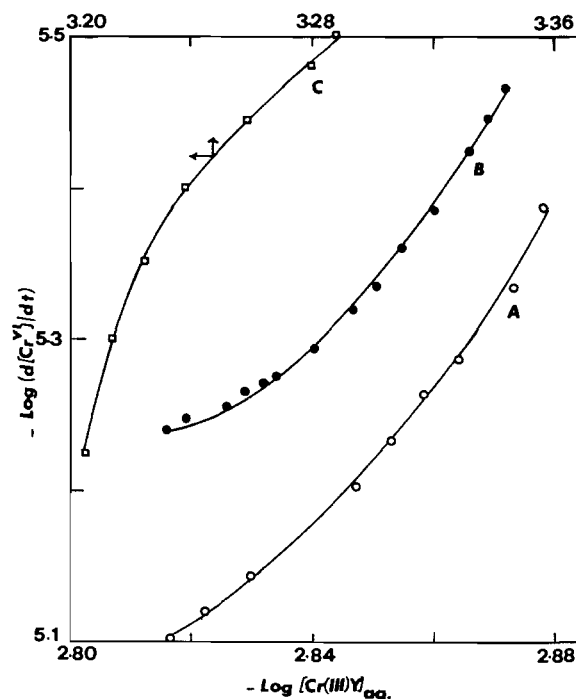

Fig. 4. Logarithmic plots of the rate of formation of CrO$_4$$^{2-}$ ion vs. the residual concentration of the chromium(III) complex under the following experimental conditions: A) [H$_2$-O$_2$] = 50.0 mmol dm^{-3}; [Cr(III)Y]$_{aq}$ = 1.549 mmol dm^{-3} and pH = 9.80; B) [H$_2$O$_2$] = 30.0 mmol dm^{-3}; [Cr(III)Y]$_{aq}$ = 1.549 mmol dm^{-3} and pH = 9.80; C) [H$_2$O$_2$] = 50.0 mmol dm^{-3}; [Cr(III)Y]$_{aq}$ = 0.641 mmol dm^{-3} and pH = 9.80.

are non-linear, which made it difficult to assign a particular dependency on [Cr(III)] for this side reaction.

Catalytic Decomposition of H_2O_2 in the pH Range 5-8

In this pH range, the aquo- and monohydroxo complexes are the predominent species. At fixed concentration of $[Cr(III)Y]_{aq}$ $(1.549 \times 10^{-3}$ mol dm^{-3}) and H_2O_2, the dependence of the hydrogen ion concentration can be accounted for by the following rate equation,

$$Rate = -d[H_2O_2]/dt$$
$$= \frac{k_1 + k_2 K_1 [H^+]^{-1}}{1 + K_1 [H^+]^{-1}} [Cr(III)Y]_{aq}[H_2O_2] \quad (7)$$

where k_1 and k_2 are the rate constants for the reactions of the aquo- and monohydroxo complexes respectively.

The kinetic data were fitted to eqn. 7 taking K_1 as an additional parameter. Best fit was obtained with $pK_1 = 7.22$ (at 30 °C) which is in fair agreement with that reported in the literature (7.39 at 20 °C) under comparable experimental conditions. Figure 5 presents the linear plots of k_{obs} $(1 + K_1[H^+]^{-1})$ against $K_1[H^+]^{-1}$ at the different temperatures studied and Table III summarises all the rate constants obtained, together with the calculated activation parameters.

Equation 7 predicts a two-pathway reaction for the decomposition of hydrogen peroxide; each is first-order in chromium and peroxide concentrations, and one of which is inversely proportional to $[H^+]$. Accordingly,
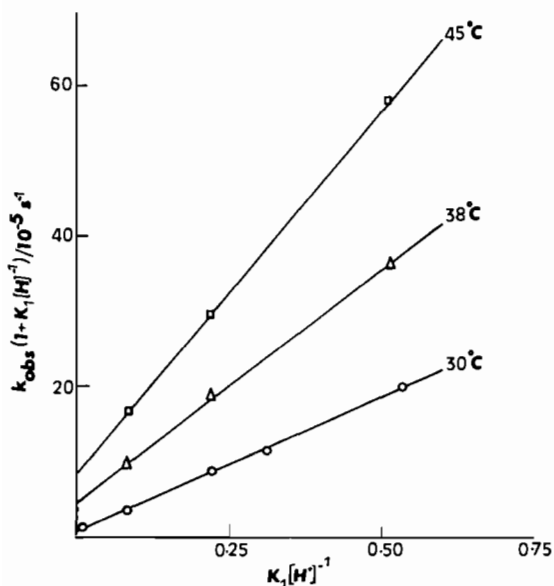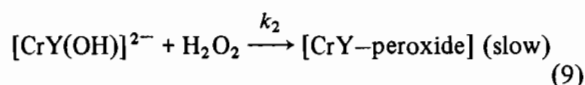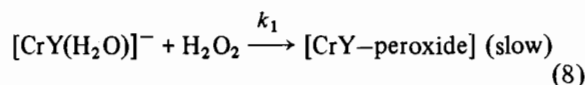

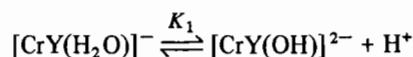Fig. 5. The linear dependency of k_{obs} $(1 + K_1(H^+)^{-1})$ on the function $K_1[H^+]^{-1}$ at the different temperatures studied.
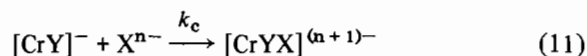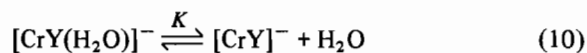
TABLE III. A Summary for the Activation Parameters for the Catalytic Decomposition of H_2O_2 in the Presence of $[Cr(III)Y]_{aq}$.

Temperature (°C)	$k_1/10^{-2}$ (dm^3 mol^{-1} s^{-1})	k_2 (dm^3 mol^{-1} s^{-1})
30	1.749	0.174
38	3.176	0.393
45	5.481	0.624

$\Delta H_1^{\ddagger} = 58.9$ kJ mol^{-1}; $\Delta S_1^{\ddagger} = -85$ J mol^{-1} deg^{-1}
$\Delta H_2^{\ddagger} = 66.5$ kJ mol^{-1}; $\Delta S_2^{\ddagger} = -40$ J mol^{-1} deg^{-1}

$$[CrY(H_2O)]^- \underset{}{\overset{K_1}{\rightleftharpoons}} [CrY(OH)]^{2-} + H^+$$

$$[CrY(H_2O)]^- + H_2O_2 \xrightarrow{k_1} [CrY-peroxide] \text{ (slow)} \quad (8)$$

$$[CrY(OH)]^{2-} + H_2O_2 \xrightarrow{k_2} [CrY-peroxide] \text{ (slow)} \quad (9)$$

These peroxo intermediates can be formed by either a peroxide—water (or hydroxo) exchange or by substituting a peroxide molecule for one of the coordinated carboxylate groups, thus resulting in the formation of a quadridentate EDTA—peroxo complex.

Previously it has been demonstrated that an uncoordinated carboxylate group attached to an existing ligand has a remarkable labilising effect on the substitution properties of chromium(III) metal complexes. Ogino *et al.* [27] showed that with the quinquedentate Cr—EDTA complex there is a rapid equilibration with acetate ligand (replacement of a coordinated H_2O by CH_3COO^- anion), whereas with the structurally-related quinquedentate Cr—MEDTA (MEDTA = N-methyl-ethylenediamine-NN'N'-triacetic acid), the methyl group is unable to labilise the coordinated water molecule. The labilisation effect of the carboxylate group was attributed to a transient sexidentate coordination of EDTA [26]. The substitution reaction takes place in two stages,
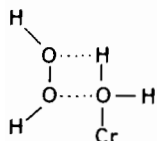
$$[CrY(H_2O)]^- \overset{K}{\rightleftharpoons} [CrY]^- + H_2O \quad (10)$$

$$[CrY]^- + X^{n-} \xrightarrow{k_c} [CrYX]^{(n+1)-} \quad (11)$$

and each step proceeds through an intramolecular associative process. The cumulative constant Kk_c, was estimated to be 3.3 dm^3 mol^{-1} for X = acetate [27] and 98 dm^3 mol^{-1} s^{-1} for the stronger nucleophile azide ligand [26]. Since there is a less favourable electrostatic factor in the case of H_2O_2 sub-

stitution, the most likely conclusion is a slower rate, as is the case with the k_1 term in this study. However, the value of k_2 is approximately one order of magnitude faster than k_1 and since the OH^- group is generally a poor leaving group compared to H_2O, it follows that the equilibration reaction possibly proceeds through substitution of the H_2O_2 nucleophile for one of the coordinated carboxylate groups. The enhanced effect observed with the monohydroxo complex would perhaps be attributed to an assisted labilisation of the coordinated hydroxo group. A comparison of the results observed with those obtained for a quinquidentate to a quadridentate conversion supports this conclusion. For example, the reaction,
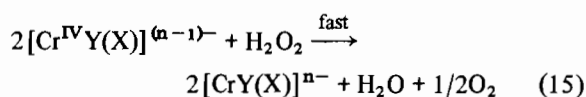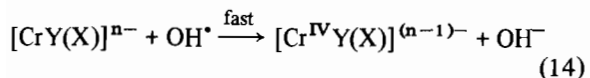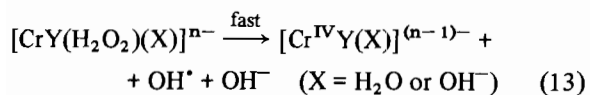
$$[CrY(OH)]^{2-} + X \longrightarrow [CrYX(OH)]^{2-} \qquad (12)$$

has a rate constant of 4.8×10^{-3} s^{-1} for X being a water molecule [24] compared to 2.7×10^{-4} s^{-1} for X being a peroxide molecule. Further support for the proposed mechanism is found in the similarities of enthalpies of activation for both the acid-dependent and acid-independent mechanisms. This suggests that bond-breaking and bond-formation processes are taking place through a common entering (H_2O_2) and leaving (coordinated $-COO^-$) group. Also, these values match that reported for reaction 12 when X is taken as H_2O molecule ($\Delta H^* = 72.8$ KJ mol^{-1} [24]).

On the other hand, the relatively large and negative activation entropy is also consistent with a mechanism where the Cr$-$O bond is intact. The following intermediate (one proton less for the

hydroxo derivative) could form and yield the peroxo compound after proton rearrangement and elimination of H_2O (or OH^-). The difference between ΔS^* and ΔS_2^* could be due to an intramolecular hydrogen bond (possible with H_2O as ligand, impossible with OH^-) which restricts the rotational freedom of H_2O_2. Both explanations are equally possible and it is difficult to differentiate between them.

For the subsequent reactions, the following schemes are suggested,

$$[CrY(H_2O_2)(X)]^{n-} \xrightarrow{\text{fast}} [Cr^{IV}Y(X)]^{(n-1)-} +$$
$$+ OH^{\bullet} + OH^- \quad (X = H_2O \text{ or } OH^-) \qquad (13)$$

$$[CrY(X)]^{n-} + OH^{\bullet} \xrightarrow{\text{fast}} [Cr^{IV}Y(X)]^{(n-1)-} + OH^-$$
$$\qquad (14)$$

$$2[Cr^{IV}Y(X)]^{(n-1)-} + H_2O_2 \xrightarrow{\text{fast}}$$
$$2[CrY(X)]^{n-} + H_2O + 1/2 O_2 \qquad (15)$$

Alternatively, two-electron transfer reactions may take place leading to the formation of chromium(V) intermediates. ESR evidence obtained in a study of the oxidation of $Cr(H_2O)_6^{3+}$ ion by hydrogen peroxide revealed that in the presence of strong chelating agents such as ethylenediamine (the latter by occupying sites on the metal ion) inhibits the coordination of a second peroxide ligand, thereby favouring the production of Cr(IV) at the expense of Cr(V) [28].

Experimental

All reagents were of AnalaR grade. A sample of the complex $[Cr(HY)(H_2O)]$ was prepared and characterised as described elsewhere [22]. The purity of the compound was checked by analysing for the chromium contents and also spectrophotometrically (λ_{max} 390 nm, ϵ_{max} 61 dm^3 mol^{-1} cm^{-1} and λ_{max} 590 nm, ϵ_{max} 87 dm^3 mol^{-1} cm^{-1} for solutions buffered at pH 9.8).

All measurements were obtained in a constant ionic strength medium of $\mu = 0.10$ mol dm^{-3} (KNO$_3$). The hydrogen ion concentration was determined using a Radiometer pH-meter model M 62 fitted with a combined glass-calomel electrode. The activity coefficient was taken as 0.782. Absorption spectra were recorded on a Unicam SP 1800 spectrophotometer thermostated to 303 K by means of a circulating constant-temperature water through a sealed jacketed cell.

Kinetics

The rate of formation of CrO_4^{2-} was monitored spectrophotometrically at 372 nm. The concentration of $[Cr(III)Y]_{aq}$ was varied from 0.64 to 1.55 mmol dm^{-3} with the concentration of hydrogen peroxide being in a minimum of 19-fold excess. The rate of disappearance of hydrogen peroxide was followed iodometrically. The details of the iodometric procedure are essentially the same as described previously [8].

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