Kinetics of the Oxidation of Ethylenediaminetetraacetato and *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetato Complexes of Cobalt(II) by Hydrogen Peroxide in Aqueous Acidic Medium

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Kinetics of the oxidation of Co(II) complexes, $Co(edta)^{2-}$ and $Co(hedta)^{-}$ [H_4edta=ethylenediaminetetraacetic acid and H_3hedta=*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid] have been studied in aqueous acidic medium (pH 3.6—4.8) at 30—60 °C. The reactions were shown to exhibit second-order kinetics, first-order in each of the reactants. In the pH range studied, the rates of reaction showed inverse $[H^+]$ dependence which could be accounted for in terms of the acid-base equilibrium $H_2O_2 \overset{K_a}{\rightleftharpoons} HO_2^- + H^+$. Applying the limiting conditions $[H^+] \gg K_a$, $[H_2O_2] \gg [HO_2^-]$, the rate-law is given by $d[Co^{III}\text{-}L]/dt = 2\{k_{H_2O_2} + k_{HO_2^-} K_a [H^+]^{-1}\} [Co^{II}\text{-}L] [H_2O_2]$ where L denotes the general form of the ligand in either case. At 30 °C (I, 0.5 mol dm^{-3}), values obtained are $k_{H_2O_2} = (5.6 \pm 0.3) \times 10^{-5}$ mol^{-1} dm^3 s^{-1}, $k_{HO_2^-} = (5.4 \pm 0.3) \times 10^2$ mol^{-1} dm^3 s^{-1} for the $Co(edta)^{2-}$ complex and $k_{H_2O_2} = (4.5 \pm 0.4) \times 10^{-5}$ mol^{-1} dm^3 s^{-1}, $k_{HO_2^-} = (5.1 \pm 0.5) \times 10^2$ mol^{-1} dm^3 s^{-1} for the $Co(hedta)^{-}$ complex. The corresponding activation parameters are $\Delta H^* = (71 \pm 8)$ kJ mol^{-1}, $\Delta S^* = -(92 \pm 23)$ J K^{-1} mol^{-1} ($Co(edta)^{2-}$ system) and $\Delta H^* = (89 \pm 2)$ kJ mol^{-1} and $\Delta S^* = -(36 \pm 4)$ J K^{-1} mol^{-1} ($Co(hedta)^{-}$ system).

Redox reactions of hydrogen peroxide have been studied earlier by a number of workers.[1] In view of the resemblance of hydrogen peroxide reactions with the biologically relevant reactions of catalase and peroxidase,[2,3] peroxide reactions are of topical interest. The present kinetic study of the oxidation reactions of $Co^{II}(edta)^{2-}$ and $Co^{II}(hedta)^{-}$[H_4edta= ethylenediaminetetraacetic acid and H_3hedta=*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid] with hydrogen peroxide was carried out because of the general interest in redox reactions of hydrogen peroxide, and also due to the fact that marked differences in the reactivity between various coordination complexes with hydrogen peroxide are generally observed.

Experimental

Materials. The Co^{II}–edta solution was prepared by adding a little excess (≈10%) of the requisite amount of Na_2H_2edta to the Co(II) solution. Preparation of Co^{II}–hedta and buffers has been described elsewhere.[4] Stabilizer-free hydrogen peroxide (BDH) was distilled under vacuum, and its concentration was checked by titration with standard $KMnO_4$. Ionic strength of the solutions were adjusted with KNO_3. All chemicals were of reagent grade.

Measurements. pH measurements were done with a Beckman digital pH meter (4500) and a Pye-Unicam recording spectrophotometer (SP8-150) was used for the measurements of absorption spectra. Kinetics were followed on a Hilger Uvispek machine as mentioned earlier.[4]

Results

Kinetics of the Oxidation of Co^{II}–edta and Co^{II}–hedta with H_2O_2. When aqueous solutions of the Co(II) complexes were mixed with that of hydrogen peroxide, intense coloration developed slowly. No rapid reaction as revealed by spectral features was observed.

The stoichiometry of the reactions corresponding to the slow change was determined as follows. Solutions containing the Co(II) complexes of concentration greater than twice the concentration of hydrogen peroxide (in each case) were kept at 50 °C for 24 h, and the amounts of Co(III) product formed were estimated from the ε_{max} values at 380 and 535 nm for the Co^{III}–edta complex, and at 380 and 550 nm for Co^{III}–hedta complex. One mole of the oxidant was consumed per two moles of the Co(II) complexes. Under our experimental conditions (pH 3.6—4.8), Co(III) complexes are formed quantitatively. Spectral data reveal that the product of oxidation for the Co^{II}–hedta complex is not the sexidentate species Co(hedta), but the quinquedentate species, $Co(hedta)H_2O$. Earlier studies[4] carried out by us on the oxidation of Co^{II}–hedta by peroxodisulfate ion show the formation of the identical species. Sulfab[5] also claims the formation of the quinquedentate species in course of the oxidation studies of Co^{II}–hedta with periodate in the pH range 4.0—4.8. Kinetics of both the reaction systems were studied at 30—60 °C using large excess of hydrogen peroxide over the Co(II) complexes. The conventional first-order plots log $(A_\infty - A_t)$ *vs.* time(t) are linear for at least three half-lives of the reactions. This shows that the oxidation reactions are first-order dependent on the Co(II) complex concentration. Plots of k_{obsd} *vs.* $[H_2O_2]$ gave good straight lines passing through zero. This shows that the reactions are also first-order with respect to the oxidant (Fig. 1). The rate-law for the oxidation of Co^{II}–edta and Co^{II}–hedta by H_2O_2 is thus represented by Eq. 1:

$$\frac{d[Co^{III}\text{-}L]}{dt} = 2k[Co^{II}\text{-}L][H_2O_2], \quad (1)$$

where L is the abbreviated form of the ligand in each case (the charges for the complexes have been omitted for brevity) and k is the second-order rate constant. Values of k determined from the slopes of plots of the type shown in Fig. 1 for both the systems are shown in Table 1. ΔH^* and ΔS^* values obtained from least-squares fit to Eyring equation are also shown in Table 1.

The effect of pH on the redox reactions was also

investigated in the range 3.6—4.8 (at a fixed peroxide concentration). Both the complexes exhibited an inverse $[H^+]$ dependence which indicates the occurrence of an acid-base equilibrium. It is well-known that hydrogen peroxide is a weak acid, dissociation of which is governed by an equilibrium of the type,

$$H_2O_2 \overset{K_a}{\rightleftharpoons} HO_2^- + H^+. \quad (2)$$

($K_a = 2.6\times10^{-12}$ mol dm^{-3} at 30 °C[6])

Under the present conditions of kinetic study where $[H^+] \gg K_a$, the predominant reacting species is obviously molecular hydrogen peroxide ($[HO_2^-] \ll [H_2O_2]$). The second-order rate constant (defined by $k_{obsd}/2[H_2O_2]$) is therefore given by:

$$k = k_{H_2O_2} + k_{HO_2^-}K_a[H^+]^{-1}, \quad (3)$$

where $k_{H_2O_2}$ and $k_{HO_2^-}$ denote the rate contributions due to hydrogen peroxide and hydrogen peroxide ion respectively. Values of $k_{H_2O_2}$ and $k_{HO_2^-}$ can be extracted from plots of k *vs.* $K_a[H^+]^{-1}$. Such plots (at 30 °C) gave excellent linearity with slopes and intercepts (Fig. 2), and the computed values are listed in Table 2. The reactivity of HO_2^- is $\approx 10^7$ times

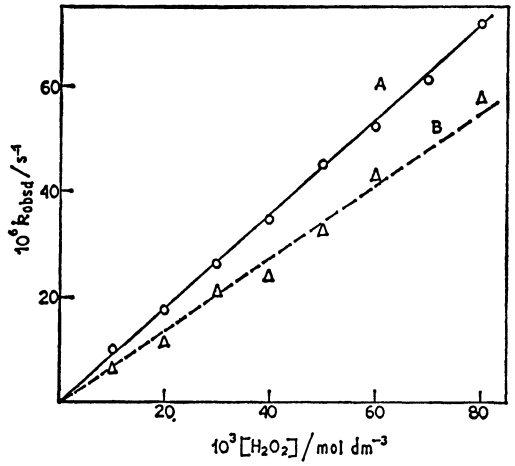

Fig. 1. k_{obsd} *vs.* $[H_2O_2]$ plot at 50 °C.
[Complex]: 0.001 mol dm^{-3}, I: 0.5 mol dm^{-3}, pH: 4.0. A: Co^{II}–edta (○), B: Co^{II}–hedta (△).

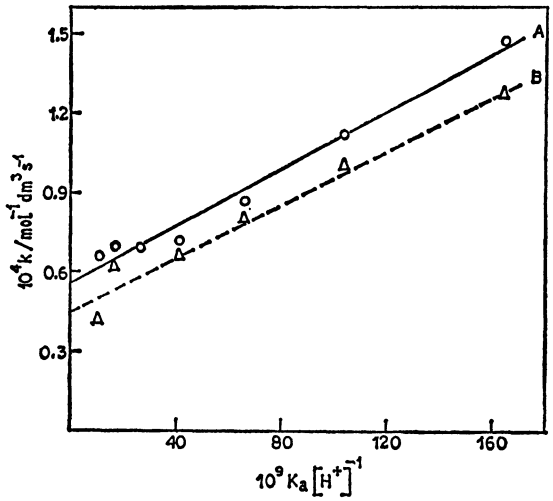

Fig. 2. Plot of k *vs.* $K_a[H^+]^{-1}$ at 30 °C.
[Complex]: 0.001 mol dm^{-3}, $[H_2O_2]$: 0.08 mol dm^{-3}, I: 0.5 mol dm^{-3}. A: Co^{II}–edta (○), B: Co^{II}–hedta (△).

Table 1. Rate constants[a] and activation parameters for the oxidation of Co^{II}–edta and Co^{II}–hedta with H_2O_2

Complex ion[b]	Temp/°C[c]	k / 10^{-4} mol^{-1} dm^3 s^{-1}	ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}
$Co^{II}(edta)^{2-}$	40	1.61±0.05	71±8	−92±23
	50	4.48±0.1		
		4.45±0.28[d]		
	60	8.74±0.26		
$Co^{II}(hedta)^-$	40	1.15±0.01	89±2	−36± 4
	50	3.40±0.3		
		4·08±0.06[d]		
	60	9.53±0.25		

a) pH, 4.0 (NaOAc+HOAc); I, 0.5 mol dm^{-3} (KNO_3+NaOAc). b) Kinetics were followed at 535 nm for the $Co^{II}(edta)^{2-}$ complex. For $Co^{II}(hedta)^-$, these were measured at 550 nm. For the evaluation of k, six to eight sets of experiments at various hydrogen peroxide concentrations were carried out. The k_{obsd} value for each set is again obtained as the average of two or three repetition which were within ±3%. c) Temperature control was within ±0.1 °C in the thermostatic bath. d) pH, 4.0; I, 1.0 mol dm^{-3}.

Table 2. Kinetic parameters[a] obtained from pH variation studies on the oxidation of $Co^{II}(edta)^{2-}$ and $Co^{II}(hedta)^-$ by hydrogen peroxide

Complex ion	$k_{H_2O_2}$ / 10^{-5} mol^{-1} dm^3 s^{-1}	$k_{HO_2^-}$ / 10^2 mol^{-1} dm^3 s^{-1}	$k_{HO_2^-}/k_{H_2O_2}$
$Co(edta)^{2-}$	5.6±0.3	5.4±0.3	9.6×10^6
$Co(hedta)^-$	4.5±0.4	5.1±0.5	11.3×10^6

a) Temp, 30 °C; I, 0.5 mol dm^{-3}; $[H_2O_2]$, 0.08 mol dm^{-3}. Values have been obtained by linear regression analysis of the data and errors shown are standard deviations.

higher than that of H_2O_2 in either case.

Discussion

In most of the reactions of hydrogen peroxide studied earlier one-electron oxidation and formation of radicals are observed.[7] On the basis of our experimental data, it is quite reasonable to believe that the present reaction systems follow the general scheme (Eqs. 4—6) in which H_2O_2 and HO_2^- are both involved in bimolecular rate-determining steps with $Co^{II}L$,

$$Co^{II}L + H_2O_2 \xrightarrow[k_{H_2O_2}]{\text{slow}} Co^{III}L + OH^- + OH\cdot, \quad (4)$$

$$Co^{II}L + OH\cdot \xrightarrow{\text{fast}} Co^{III}L + OH^-, \quad (5)$$

$$Co^{II}L + HO_2^- \xrightarrow{k_{HO_2^-}} \text{Products}. \quad (6)$$

The free radical mechanism, namely (4)—(5) is well supported by experimental evidences gathered over the last few years[8-10] (specially using the ESR technique[1]). The electron transfer step expressed in Eq. 6 could be followed by a precursor equilibrium between the substrate and HO_2^-. The criterion for such an equilibrium under the present conditions must be that it is significantly small. Furthermore, the equilibrium must be obtained fairly rapidly compared to the intramolecular electron transfer step, else saturation of the pseudo-first-order rate constant would have been observed at high concentration of hydrogen peroxide. Sutin[11] has also put forward evidence for an HO_2^- path in course of kinetic studies of the reaction of chromium(II) cyanide complexes with hydrogen peroxide in aqueous solution. The rate-determining intramolecular electron transfer is preceded by an association step as:

$$Cr(CN)_5H_2O^{3-} + HO_2^- \overset{K_a}{\rightleftharpoons} [\text{Complex}]^{3-} + CN^-, \quad (7)$$

$$[\text{Complex}]^{3-} \xrightarrow{k} \text{Products}. \quad (8)$$

Yalman[12] has studied the electron transfer reaction of Co^{II}–edta with hydrogen peroxide in the pH range 6.5—8.5 by manometric, spectrophotometric, and polarographic techniques. A peroxodicobalt(III, III) intermediate, (edta)CoOOCo(edta)$^{4-}$ having an intense band in the ultraviolet region is claimed to be formed, the formation of which is supported by polarographic measurements. In the present study where the pH has been kept below 4.8, no spectral evidence could be gathered for the formation of any intermediate species. However, our earlier studies[4] on the electron transfer reaction of Co^{II}–hedta with peroxodisulfate ion present the opportunity for detection of an intermediate which is believed to be a mononuclear Co^{III} complex containing the oxidant (in part) in the inner-sphere.

The reactivity of the two complexes towards peroxide oxidation is more or less the same (the Co^{II}–edta complex reacting little faster than the Co^{II}–hedta complex). However, a fairly large difference in the entropy of activation (Table 1) is found for the two reaction systems which may originate from the difference in charge on the Co(II) complexes. Positively charged complexes reacting with HO_2^- are expected to have the least negative entropies of activation due to charge neutralization in the transition state leading to desolvation. Neutral and negatively charged complexes will have more negative entropies because of developing charge in the transition state.[13] The activation energies for these reactions are considerably lower than the value of 140 kJ required for the symmetrical fission of the peroxide bond[1] and may be rationalized as a stabilization of the activated complexes caused by partial transfer of electrons from the metal ion to a 'generating' hydroxyl radical ion.

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