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Kinetics of the Decomposition of Hydrogen Peroxide in the Presence of Ethylenediaminetetraacetatocerium(IV) Complex

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Abstract

The rate of reaction of $[Ce(EDTA)(OH)_n{}^{n-}]$ with H_2O_2 in 0.10 M KNO_3 solution was investigated at various temperatures. The presence of a peroxy intermediate is inferred from spectrophotometric measurements. The general rate equation,

$$-d[H_2O_2]/dt = \frac{k_1 + k_2K_1[H^+]^{-1}}{(1 + K_1[H^+]^{-1})(1 + K_2{}^{-1}[H^+]^{-1})} \times [Ce(EDTA)(OH)_n{}^{n-}][H_2O_2]$$

is valid for pH 7–9 with $n = 1$ and 2 complexes involved. The rate constants k_1 and k_2 were determined at 25 °C to be 0.054 and 0.171 M^{-1} s^{-1} respectively. The corresponding activation enthalpies, as calculated from Arrhenius plots, were $\Delta H_1{}^{\#} = 51.3 \pm 14.8$ and $\Delta H_2{}^{\#} = 41.8 \pm 5.3$ kJ m^{-1} and the activation entropies were $\Delta S_1{}^{\#} = -97 \pm 47$ and $\Delta S_2{}^{\#} = -119 \pm 17$ J $K^{-1} m^{-1}$.

Introduction

The redox reactions of hydrogen peroxide with aquo metal cations such as Mn(III) [1], Fe(III) [2], Co(III) [3] and Ag(II) [4] have been studied rather extensively. The general mechanism involves rapid formation of intermediate complexes such as $M(H_2O_2)$ and $M(O_2H^-)$. In this paper, interest is directed to the reactions involving Ce(IV) complexed with EDTA.

The Ce(IV) + H_2O_2 reaction has been assumed to proceed through two consecutive electron transfer reactions [5, 6]. In concentrated sulfate medium where $Ce(SO_4)_3{}^{2-}$ was the dominant species the reaction was described by steps (1) and (2) [7, 8].

$$Ce(IV) + H_2O_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ce(III) + HO_2^{\bullet} + H^+ \qquad (1)$$

$(k_f = 10^6\ M^{-1}\ s^{-1})$

$$Ce(IV) + HO_2^{\bullet} \xrightarrow{k_2} Ce(III) + O_2 + H^+ \qquad (2)$$

$(k_b[H^+]/k_2 = 0.129)$

The overall stoichiometry involved reduction of 2 mol Ce(IV) per mol of H_2O_2. The presence of the $HO_2^{\bullet}$ radical inferred in this mechanism was affirmed subsequently by ESR measurements [9]. The O_2 produced was shown to be entirely from H_2O_2 origin by O^{18} tracer measurements [10]. Wells and Hussain [11] proposed the rapid formation of the intermediate species, $Ce(H_2O_2)^{4+}$ and $Ce(O_2H)^{3+}$ by the reactions (3)–(5):

$$Ce^{4+} + H_2O_2 \overset{\beta_1}{\rightleftharpoons} Ce(H_2O_2)^{4+} \qquad (3)$$

$$Ce(H_2O_2)^{4+} \overset{K}{\rightleftharpoons} Ce(O_2H)^{3+} + H^+ \qquad (4)$$

$$Ce(OH)^{3+} + H_2O_2 \overset{\beta_1{}'}{\rightleftharpoons} Ce(O_2H)^{3+} + H_2O \qquad (5)$$

These reactions are followed by the rate determining electron-transfer steps. The evidence for the existence of peroxo intermediates was inferred from optical density changes at 350 nm. These authors also attributed the absence of the back reaction in step (1) in perchlorate media (in contrast to its presence in sulfate media) to the difference in the redox potential of the Ce(IV)/Ce(III) couple in the two systems. Samuni and Czapski [12], however, attributed this difference in reaction to the presence of a small percentage of polymeric cerium(IV) species in the perchlorate solution. It would seem likely that the stronger complexation by sulfate ion shifts the equilibrium of reaction (1) to the left in agreement with the interpretation of Wells and Hussain [11].

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The latter explanation is supported by the observation that peroxide decomposition reaction is significantly retarded in the presence of chelate complexes and is completely inhibited in the absence of 'free' coordination sites in the coordination sphere [13–15]. An additional redox requirement is the ability of the metal ion to exist in two or more different oxidation states of reasonable stability [13].

Earlier studies of aminopolycarboxylate complexes as catalysts for H_2O_2 disproportionation were limited to vanadium [16], chromium [17], manganese [18] and iron [19] systems. The results obtained are consistent with substitution controlled mechanisms through the formation of the ternary peroxo complexes. To investigate this model with a catalyst complex of strongly ionic character, we have studied the decomposition of H_2O_2 with the ethylenediaminetetraacetatocerium(IV) complex.

Experimental

Reagents

All solutions were prepared with deionized water. Ammonium hexanitratocerate(IV) (A.R.) and hydrogen peroxide (30%) (A.R.) were obtained from J. T. Baker Chemical Co. Stock solutions of the reagents were prepared and standardized iodometrically [20]. EDTA solutions were prepared as the tetrasodium salt using the Aldrich reagent. Carbonate free-sodium hydroxide was used in all experiments to adjust the pH of the medium and analytical grade potassium nitrate solution was used to adjust the ionic strength to a fixed value (0.10 M unless otherwise specified).

Kinetic Measurements

Appropriate amounts of Ce(IV), EDTA and NaOH solutions were mixed and the resulting yellow solution adjusted to 0.10 M ionic strength with KNO_3. The EDTA was always more than twice the equivalent amount of cerium. This preparation was found adequate to avoid hydrolysis of the Ce(IV) cation at higher pH values while the excess EDTA served as a pH buffer [17, 19a]. The mixture was thermostatted to the proper temperature and the reaction initiated by an injection of a precalculated amount of the stock solution of H_2O_2. Aliquots were removed periodically and their reaction quenched by addition to a $KI + H_2SO_4$ solution. The residual amount of peroxide in these samples was determined iodometrically. The pH of the solution was also monitored during each kinetic run using a Corning pH meter 130 fitted with a combined glass-calomel electrode which had been standardized with two buffers over the desired pH range.

Spectral Measurements

Spectral measurements were obtained using both Cary 14 (UV–Vis spectrophotometer) and Tracor Northern TN-6050 spectrophotometer fitted with Tracor Northern TN-1710 multichannel analyzer and Omnigraphic 2000 recorder (Houston Instruments). In all measurements, 1 cm matched cells were used where water or Ce(EDTA) solution served as the blank.

Results and Discussion

Addition of Na_4EDTA to an equimolar amount of ceric nitrate results in the formation of the sparingly soluble [Ce(EDTA)] complex. The latter can be dissolved in a stoichiometric amount of sodium hydroxide by forming the ternary $[Ce(EDTA)(OH]^{1-}$ species. The hydrolysis constant for formation of this species has been determined spectrophotometrically over the pH range 2–4 and estimated to be 11.16 [21]. Our potentiometric measurements are consistent with the presence of a second buffer region in the pH range 5–7 with the apparent hydrolysis constant $\log K = -7.8$ for the reaction,

$$[Ce(EDTA)(OH)^{1-}] + H_2O \rightleftharpoons [Ce(EDTA)(OH)_2{}^{2-}] + H^+ \quad (6)$$

The uncertainty in this value is relatively high due to the problems of stability of the electrode in this pH range. This bishydroxo complex absorbs at 366.2 nm with an ϵ_{max} of 230 M^{-1} cm^{-1} (Fig. 1). The possibility of autoreduction of Ce(EDTA) species to Ce(III) was ruled out since the absorbance of the hydroxo complex remained virtually the same over two hours which was the duration of a typcial kinetic run.

Addition of hydrogen peroxide to this mixture was accompanied by an intense color change to

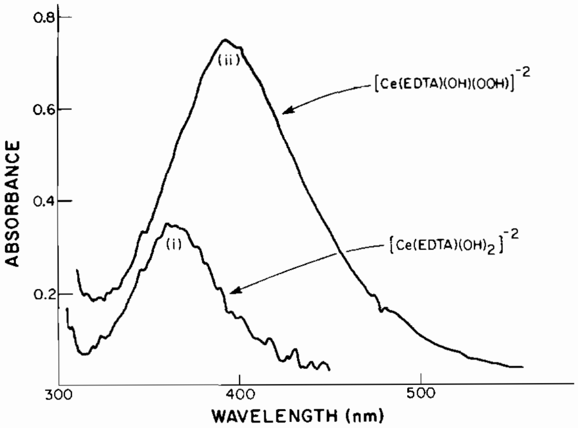


Fig. 1. Absorption spectra of cerium–EDTA in (i) the absence and (ii) the presence of hydrogen peroxide ($I = 0.10$ M KNO_3; $T = 25$ °C).

orange–red presumably due to formation of an H_2O_2 complex. Poluektov *et al.* [22] and Bogdanovich *et al.* [23] have suggested the presence of ternary complexes in solution between lanthanides-aminopolycarboxylates and hydrogen peroxide with 1:1 stoichiometry. A similar 1:1 intermediate was detected in the case of iron(III) [19]. Solid complexes with the stoichiometries $K[Ln(EDTA)(H_2O_2)_{0.5}]\cdot 6H_2O$ (**A**), $K_3[Ln(O_2)(EDTA)]\cdot 6H_2O$ (**B**), and $K_3[Ln(O_2)(EDTA)(H_2O_2)]\cdot 5H_2O$ (**C**) have been isolated [24]. Thermal analysis of compound **C** was interpreted as indicating only the peroxide ion to be strongly bound to the lanthanide ion. Compounds **B** and **C** can be formulated as $K_3[Ln(OOH)(OH)(EDTA)]\cdot X\cdot 4H_2O$ where X is H_2O_2 for compound **B** and H_2O for compound **C**.

In solution, the peroxo ceric complex absorbed at 394.8 nm with a molar absorptivity, $\epsilon_{max} = 1015$ M^{-1} cm^{-1} (Fig. 1b). The yellow color of hydroxo-EDTA complex was still present after completion of the H_2O_2 decomposition. Preliminary experiments on the formation of the red–orange intermediate showed that the reaction was 90% complete within the first two minutes when the cerium concentration was 0.2 mM and there was a 10 fold excess of hydrogen peroxide.

Pseudo first order conditions were maintained in all runs by using a large excess of hydrogen peroxide over cerium. Figure 2 presents examples of the plots of the residual peroxide concentration as a function of time and at different pH values. Plots of the $\log[H_2O_2]$ *versus* time were linear until the reaction was at least 75% complete at which time the ratio $[H_2O_2]/[Ce(EDTA)(OH)_n{}^{n-}] \geq 4.0$. A sample of these plots is given in Fig. 3. At a prefixed condition of pH, temperature and $[H_2O_2]$, the observed rate constant is directly proportional to the total cerium as shown in Fig. 4. Accordingly, the rate of disproportionation of the peroxide may be given by:

$$-d[H_2O_2]/dt = k_{obs}[H_2O_2][Ce(EDTA)(OH)_n{}^{n-}] \quad (7)$$

where

$$[Ce(EDTA)(OH)_n{}^{n-}] = [Ce(EDTA)(OH)^{1-}] + [Ce(EDTA)(OH)_2{}^{2-}] \quad (8)$$

The dependency on pH of the decomposition reaction was studied between 25 and 45 °C at fixed concentrations of $[H_2O_2]$ and $[Ce(EDTA)(OH)_n{}^{n-}]$. The formation of colloidal cerium above pH 9.2 set this as the upper pH limit of the kinetic measurements. Figure 5 shows the plots of k_{obs} *versus* pH at the different temperatures. The sigmoidal shape of these relationships suggests that one of the reactants is involved in acid–base equilibria in this pH range with a log $K \simeq 8$. Based on the value we measured previously of 7.8, the acid–base reaction is assumed to be that of eqn. (7).

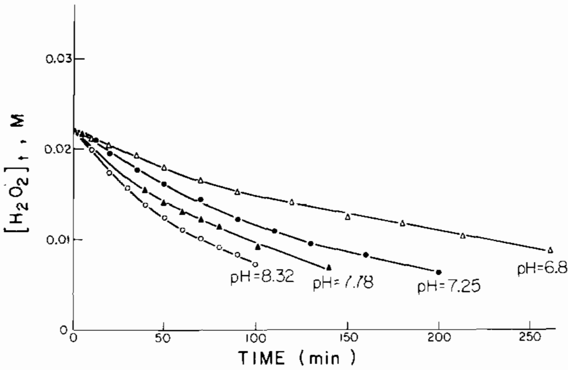


Fig. 2. Plots of the residual peroxide concentration *vs.* time at different pH values ($I = 0.10$ M KNO_3; $T = 25$ °C).

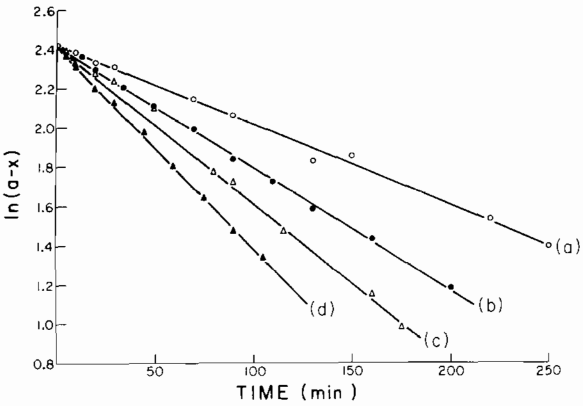


Fig. 3. Pseudo first-order plots for the decomposition of H_2O_2 in the presence of variable amounts of complexed cerium. (a) 0.864 mM, (b) 1.296 mM, (c) 1.728 mM and (d) 2.160 mM ($I = 0.10$ M KNO_3; $T = 25$ °C).

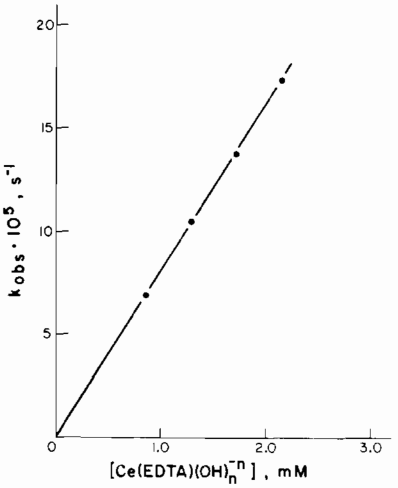


Fig. 4. Dependency of the observed rate constants on the total contents of the cerium complex ($I = 0.10$ M KNO_3; pH = 7.15).

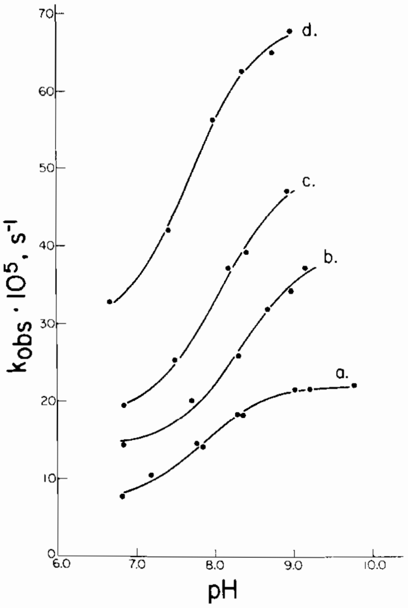


Fig. 5. The variation of k_{obs} with pH for the reaction of H_2O_2 with $[Ce(EDTA)(OH_n{}^{n-}]$ at (a) 25 °C, (b) 35 °C, (c) 40 °C and (d) 45 °C. Solid lines represent the calculated values of k_{obs} from the fitted rate constants at different pH values whereas experimental data are represented by the solid symbols.

The data are summarized in Table I. From the various experiments and the data of Table I, we can write the rate equation:

$$-d[H_2O_2]/dt = \frac{k_1 + k_2K_1[H^+]^{-1}}{(1 + K_1[H^+]^{-1})(1 + K_2{}^{-1}[H^+]^{-1})} \times [Ce(EDTA)(OH)_n{}^{n-}]\,[H_2O_2] \qquad (9)$$

where k_1 and k_2 are the rate constants for the decomposition reaction in the presence of $[Ce(EDTA)(OH)^{1-}]$ and $[Ce(EDTA)(OH)_2{}^{2-}]$ respectively. The term $(1 + K_2{}^{-1}[H^+]^{-1})$ accounts for the amount of the undissociated $[H_2O_2]$; K_2 is the protonation constant for H_2O_2. Under our experimental conditions, this term reduces to unity.

A program written by W. Cacheris based on the SIMPLEX algorithm was used to fit the equation,

$$k_{obs} = \frac{k_1 + k_2K_1[H^+]^{-1}}{(1 + K_1[H^+]^{-1})(1 + K_2{}^{-1}[H^+]^{-1})} \qquad (10)$$

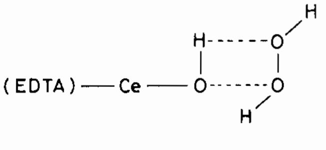
In the data treatment, the three constants k_1, k_2 and K_1 were allowed to float simultaneously. Table II lists the results of the calculations. In Fig. 5, the fit between the calculated variation of k_{obs} with pH and the experimental values is shown.

From Arrhenius plots, the activation parameters were calculated and are listed in Table II. The error limits of the activation parameters were obtained at 90% confidence following standard procedures [25]. The ionic strength effect on the reaction rate was investigated also at two different temperatures for a limited number of points. These results are presented in Table III.

TABLE I. Observed Rate Constants for the Reaction of Hydrogen Peroxide with $[Ce(EDTA)(OH_n{}^{n-}]$. $[H_2O_2]$ = 22.1 mM; I = 0.10 M (KNO_3)

$[Ce(EDTA)(OH)_n{}^{n-}]$	pH	Temperature (°C)	$k_{obs} \times 10^5\ s^{-1}$
0.864	7.20	25	6.91 ± 0.3
1.728	7.20	25	13.72 ± 0.6
2.160	7.24	25	17.31 ± 0.8
1.296	7.20	25	10.57 ± 0.5
1.296	6.83	25	7.83 ± 0.3
1.296	7.78	26	14.61 ± 0.7
1.296	7.86	25	14.15 ± 0.6
1.296	8.37	25	18.23 ± 0.8
1.296	8.30	26	18.34 ± 0.8
1.296	9.03	25	21.52 ± 1.0
1.296	9.22	25	21.52 ± 1.0
0.864	9.77	25	14.64 ± 0.6
1.296	6.85	35	14.43 ± 0.7
1.296	7.35	35	19.97 ± 0.9
1.296	7.72	35	20.13 ± 0.9
1.296	8.32	35	25.78 ± 1.2
1.296	8.70	35	31.91 ± 1.5
1.296	8.97	35	34.13 ± 1.6
1.296	9.19	35	36.96 ± 1.8
1.296	6.86	40	19.50 ± 0.9
1.296	7.52	40	25.34 ± 1.2
1.296	8.20	40	36.97 ± 1.8
1.296	8.43	40	38.91 ± 1.9
1.296	8.94	40	46.90 ± 2.3
1.296	6.68	45	32.83 ± 1.6
1.296	7.44	45	42.03 ± 2.1
1.296	7.99	45	56.22 ± 2.9
1.296	8.37	45	62.42 ± 3.2
1.296	8.75	45	64.69 ± 3.4
1.296	9.00	45	67.84 ± 3.6

In the case of cerium(IV) reduction with hydrogen peroxide, Wells *et al.* [11], attributed the observed rapid initial changes in the absorption of Ce(IV) at 350 nm to changes in the charge-transfer spectrum of the metal ion resulting from replacement of coordinated aquo or hydroxo species by $HO_2{}^{1-}$. The exchange could occur via an intermediate such as,



This intermediate then eliminates water with proton rearrangement [17]. This intermediate was proposed

TABLE II. Summary of the Activation Parameters for the Catalytic Decomposition of Hydrogen Peroxide in the Presence of $[Ce(EDTA)(OH)_n{}^{n-}]$

Temperature (°C)	k_1 ($M^{-1}\,s^{-1}$)	k_2 ($M^{-1}\,s^{-1}$)	K_1 (10^{-8})
25	0.054 ± 0.004	0.171 ± 0.002	1.85 ± 0.26
35	0.109 ± 0.010	0.306 ± 0.015	0.56 ± 0.18
40	0.138 ± 0.010	0.389 ± 0.018	1.05 ± 0.30
45	0.222 ± 0.013	0.535 ± 0.009	2.49 ± 0.47

$E_{a(1)} = 53.78 \pm 14.75$ kJ m^{-1};
$E_{a(2)} = 44.30 \pm 5.32$ kJ m^{-1};
$\Delta H_1{}^{\#} = 51.30 \pm 14.75$ kJ m^{-1};
$\Delta H_2{}^{\#} = 41.82 \pm 5.32$ kJ m^{-1};
$\Delta S_1{}^{\#} = -97 \pm 47$ J $K^{-1}\,m^{-1}$;
$\Delta S_2{}^{\#} = -119 \pm 17$ J $K^{-1}\,m^{-1}$

TABLE III. Effect of Ionic Strength on the Reaction of Hydrogen Peroxide with $[Ce(EDTA)(OH)_n{}^{n-}]$. $[Ce(EDTA)(OH)_n{}^{n-}] = 1.296$ mM; $[H_2O_2] = 22.1$ mM

Temperature (°C)	I (M)	pH	$k_{obs} \times 10^5$ (s^{-1})
25	0.215	8.27	13.88 ± 0.6
25	0.115	8.27	18.00 ± 0.8
25	0.015	8.27	14.70 ± 0.7
40	0.215	8.60	46.00 ± 2.3
40	0.115	8.60	42.70 ± 2.1
40	0.015	8.60	45.80 ± 2.3

also to account for the disproportionation of peroxide in the presence of Cr(III)EDTA [17]. The similarity of the values of the activation parameters for the Ce(IV) system to those reported previously for catalysis by Cr(III) suggests that the mechanisms of both systems may be similar. The agreement of the enthalpies in Table II also indicates that this may be the mechanism.

The rate determining step can be assigned to the formation of the ternary complex or the subsequent electron transfer process. In the latter case, the rate constants k_1 and k_2 will be a composite parameter of $K_{eq}K_{intra}$ where K_{eq} is the equilibrium constant for the formation of the peroxide complex. Unfortunately, the values of K_{eq} are not available and cannot be obtained from the present data. However, intramolecular electron-transfer rate determining reactions are associated with positive entropies which reflect the solvent reorganization upon charge redistribution [26, 27]. Taube [28] has attributed the high negative entropies (*ca.* -130 ± 12 J K^{-1} m^{-1}) in a large number of redox reactions to the fact that formation of the precursor complex is rate controlling. Based on the negative $\Delta S^{\#}$ for the present system, the following mechanism is suggested:

$$[Ce(EDTA)(OH)^{1-}] + H_2O_2 \xrightarrow[slow]{k_1} [Ce(EDTA)(O_2H)^{1-}] + H_2O \qquad (11a)$$

$$[Ce(EDTA)(OH)_2{}^{2-}] + H_2O_2 \xrightarrow[slow]{k_2} [Ce(EDTA)(O_2H)(OH)^{2-}] + H_2O \qquad (11b)$$

$$[Ce(EDTA)(O_2H)^{1-}] \longrightarrow [Ce(EDTA)^{1-}] + O_2{}^{-\bullet} + H^+ \qquad (12)$$

$$[Ce(EDTA)^{1-}] + H_2O_2 \longrightarrow [Ce(EDTA)(OH)^{1-}] + OH^{\bullet} \qquad (13)$$

$$[Ce(EDTA)(OH)^{1-}] + O_2{}^{-\bullet} \longrightarrow [Ce(EDTA)^{1-}] + O_2 + OH^- \qquad (14)$$

$$[Ce(EDTA)^{1-}] + OH^{\bullet} \longrightarrow [Ce(EDTA)(OH)^{1-}] \qquad (15)$$

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