Kinetics and Mechanism for The Oxidation of Co([15]Anen4)(H2O)22+ With Organic Hydro peroxides

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Abstract -- The kinetics for the reaction of Co([15]aneN4)(H2O)22+ with hydroperoxides were studied at μ = 0.50 M (NaClO4) in 1:1 (v/v) tert-butyl alcohol-water media. The reaction is first order in both CoII complex and hydroperoxide. The reaction rates were effected by varying the alkyl group of the hydroperoxide with the reactivity order being HOOH > C3H7(CH3)2COOH ~ C2H5(CH3)2COOH > (CH3)3COOH. Effect of ionic strength on the oxidation rate has been studied and the reaction mechanism is discussed.

Indexed Terms: Alkylcobalt complexes, Kinetics, Macrocyclic complexes

I. INTRODUCTION

Since the discovery that the stable coenzyme B12 is a cobalt (III) complex containing a σ-bonded alkyl ligand[1], there has been considerable interest in the preparation and study of analogous synthetic complexes[2-5]. The first example was several interesting organocobalt mac-N4 complexes prepared by following a photochemical reaction with Co(NH3)5O2CR2+[6, 7]. A new approach with corresponding organocobaloximes, (py)(dmgH)2CoR, as the precursor of organic radical was successfully employed to prepare organocobalt mac-N4 complexes[8-10]. The high absorption coefficients of organocobaloximes relative to those of the product organocobalt complex prevent the product itself from ready photolysis. Lippard[11] and co-workers employed the reduction of the macrocyclic CoIIN4 complexes [Co(TC-3,3)] and [Co(TC-3,4)] with 40% Na/Hg followed by addition of alkyl halide to prepare the five-coordinate Co(III) alkyl compounds. Recently, the methylcobalt(III) with classical ligand NH3, Co(NH3)5CH32+, was prepared from the reaction of CoII with methyl hydrazine in aqueous ammonia solution[12, 13]. The mononuclear cobalt(III)-peroxo complexes bearing

tetraazamacrocyclic ligands, [Co(12-TMC)(O2)]+ and [Co(13-TMC)(O2)]+, were also synthesized by reacting [Co(12-TMC)(CH3CN)]2+ and [Co(13-TMC)(CH3CN)]2+, respectively, with H2O2 in the presence of triethylamine[14]. However, alkyl cobalt(III) complexes containing solely saturated ligands have been reported only in a relatively few cases.

The reduction potential of Co([15]aneN4)(H2O)22+ is about 0.2 V higher than that of Co([14]aneN4)(H2O)22+[15].
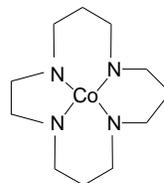
Co([15]aneN4)2+

The solution of Co([15]aneN4)(H2O)22+ is stable in neutral, but decomposed within minutes to Co2+ and free ligand upon acidification. These properties makes the aforementioned synthetic route not available for the preparation of RCo([15]aneN4)(H2O)22+. Organic hydroperoxides are used as sources of organic radicals for the preparation of organometallic complexes. In the present study the kinetics of the oxidation of Co([15]aneN4)(H2O)22+ with a series of hydroperoxides, R(CH3)2COOH, in neutral aqueous solution are reported. The mechanism of the reaction is discussed as well.

II. EXPERIMENTAL

Materials The aqueous solution of Co([15]aneN4)(H2O)2(ClO4)2 was prepared by literature method[15]. The ligand L was available (Aldrich or Across Chemical) and used directly. Organic hydroperoxides were prepared by literature methods[16-18]. All other chemicals were of reagent

grade and used without further purification. Water was purified by a Milli-Q SP system and used for all the kinetic studies.

Kinetics and spectroscopy The conventional spectrophotometric method was used for rate determinations with a Hitachi model 3000 or HP 8453 UV-visible spectrophotometer. Tert-Butyl alcohol was used to make up 1:1(v/v) tert-butyl alcohol-water solutions for all the kinetic experiments with organic hydro peroxides. A pseudo-first-order kinetic condition with hydro peroxide in excess was employed. Temperature control of □0.5 ℃ was kept by circulating water from a constant-temperature bath through the jacket of a cell holder. Ionic strength was adjusted to 0.5 M with sodium perchlorate for most the kinetic measurements otherwise as noted.

III. RESULTS AND DISCUSSION

3.1 Kinetics of the oxidation reactions The kinetic studies were conducted in 1:1 v/v tert-butyl alcohol-water at 25 ℃ in the presence of a large excess of the hydroperoxide. The rate constants of the reactions were obtained from an analysis of the increase in absorption of the products at λ 380 nm as a function of time for most hydroperoxides as shown in Figure 1. The good linear plots of ln (A∞-At) vs. time in each run showed a

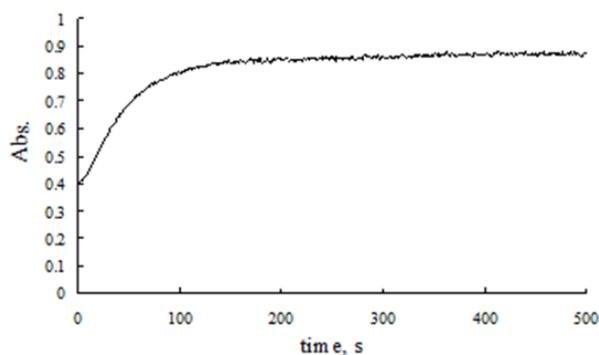Figure 1. The absorption for the reaction of Co([15]aneN$_4$)(H$_2$O)$_2$$^{2+}$ with (CH$_3$)$_3$COOH. [Co([15]aneN$_4$)(H$_2$O)$_2$$^{2+}$] = 5 x 10^{-3} M, [(CH$_3$)$_3$COOH] = 0.15 M, T=25℃, μ = 0.5 M, λ = 380 nm.

pseudo-first-order dependence on [Co([15]aneN$_4$)(H$_2$O)$_2$$^{2+}$], Figure 2. A plot of k_{obs} vs. concentration of

Figure 2. The dependence of ln(A∞-At) with time for the reaction of Co([15]aneN$_4$)(H$_2$O)$_2$$^{2+}$ with (CH$_3$)$_3$COOH. [Co([15]aneN$_4$)(H$_2$O)$_2$$^{2+}$] = 5 x 10^{-3} M, [(CH$_3$)$_3$COOH] = 0.15 M, T = 25℃, μ = 0.5 M, λ = 380 nm.

Hydro peroxide was linear and passed through the origin as shown in Figure 3. The rate law for the oxidation is

Figure 3. The dependence of pseudo-first-order rate constants on the concentration of peroxides. T = 25 ℃, μ = 0.5 M. ■ ： (CH$_3$)$_3$COOH; ● ： (C$_2$H$_5$)(CH$_3$)$_2$COOH thus

$$-\frac{d[Co([15]aneN_4)(H_2O)_2^{2+}]}{dt} = k[Co([15]aneN_4)(H_2O)_2^{2+}][peroxide]$$

where k represents the specific rate of the rate-determining step. Kinetic results for the various reactions are summarized in Table 1. The reactions of

hydrogen peroxide were treated similarly and the rate constant

Table 1. Second-order rate constants for the reaction of Co([15]aneN$_4$)(H$_2$O)$_2^{2+}$ with various peroxides[a]

peroxide	$10 \times k$, M^{-1}s^{-1}
(CH$_3$)$_3$COOH.	1.46
C$_2$H$_5$(CH$_3$)$_2$COOH	12.75
C$_3$H$_7$(CH$_3$)$_2$COOH	13.80
HOOH	84.00

[a] T = 25 ℃, μ = 0.5 M, λ = 380 nm.

is also listed in Table 1. The rate of this oxidation reaction is truly depend on the peroxide with the reactivity order being: HOOH > C$_3$H$_7$(CH$_3$)$_2$COOH ~ C$_2$H$_5$(CH$_3$)$_2$COOH > (CH$_3$)$_3$COOH. A faster reaction rate (k = 7.8 M^{-1}s^{-1}) was observed in the reaction of Co(Me$_6$[14]4,11-dieneN$_4$)$^{2+}$ with (CH$_3$)$_3$COOH owing to a lower reduction potential (E^o = 0.55 V, NHE) of Co(Me$_6$[14]4,11-dieneN$_4$)$^{2+}$[19].

3.2 The ionic strength dependence on the reaction rate

The reaction of Co([15]aneN$_4$)(H$_2$O)$_2^{2+}$ with (CH$_3$)$_3$COOH was also studied in different ionic strength. The rate constants seem like increasing with the ionic strength of the reaction medium as shown in Figure 4. The plot of log k and $\sqrt{\mu}$ gives a poor linear relation with positive slope.
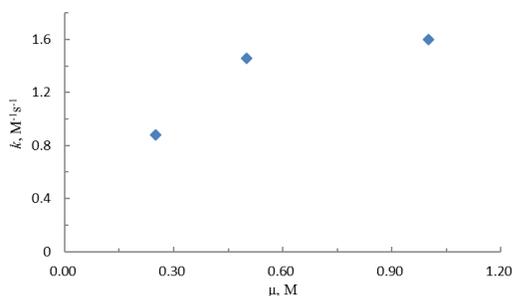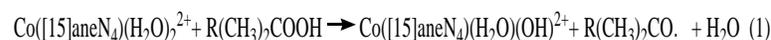

Figure 4. The dependence of ionc strength on the rate constant for the reaction of Co([15]aneN$_4$)(H$_2$O)$_2^{2+}$ with (CH$_3$)$_3$COOH. [Co([15]aneN$_4$)(H$_2$O)$_2^{2+}$] = 5 x 10^{-3} M, [(CH$_3$)$_3$COOH] = 0.15 M, T = 25 ℃.

The positive slope of the plot results in a positive z_1z_2 value in BrØnsted equation, so the transition state complex is not formed from ions with opposite charges.

3.3 The reaction mechanism The electronic spectrum of the mixture solution shows two peaks at λ 533 and 400 nm at the end. It is worthy to note that both the positions and the relative intensity of these two peaks are very similar to those of CH$_3$Co([14]aneN$_4$)$^{2+}$ (ε_{476} = 81 M^{-1}cm^{-1}, ε_{368} = 106 M^{-1}cm^{-1})[9] and other analogous[10-13]. The large scale preparation was carried for the reaction with (CH$_3$)$_3$COOH. The solid products were obtained as a perchlorate salt. The visible spectra of these products show two peaks about λ 400 and 530 nm and are consistent with that of alkyl cobalt analogous. All these results suggest the anticipated alkyl cobalt complex could probably be formed through the reaction of Co([15]aneN$_4$)(H$_2$O)$_2^{2+}$ with alkyl radical (R = CH$_3$, C$_2$H$_5$, and C$_3$H$_7$). A possible reaction mechanism is given in Scheme I by equations (1)-(3).

Scheme I

$$Co([15]aneN_4)(H_2O)_2^{2+} + R(CH_3)_2COOH \rightarrow Co([15]aneN_4)(H_2O)(OH)^{2+} + R(CH_3)_2CO. + H_2O \quad (1)$$

$$R(CH_3)_2CO. \longrightarrow (CH_3)_2CO +. R \quad (2)$$

$$Co([15]aneN_4)(H_2O)_2^{2+} +. R \longrightarrow RCo([15]aneN_4)(H_2O)^{2+} \quad (3)$$

IV. CONCLUSION

The reaction of Co([15]aneN4)(H2O)22+ with organic peroxides probably is a simple way to prepare the related alkyl cobalt complexes even though it is not successful in some cases. The products are stable in acidic aqueous solution and show no sign of decomposition within several hours of preparation.

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