Notes

The Contribution of Iron(II) Reduction Alongside Proton-induced Decomposition in the Reactions of Two μ-Hydroxo-μ-peroxo-dicobalt(III) Complexes

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It is concluded that there is little or no Fe^{2+} (10^{-3} M) reduction of the μ-hydroxo-μ-peroxo-dicobalt(III) complexes $[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$ and $[(trien)Co(OH)(O_2)Co(trien)]^{3+}$ and that the reaction observed, $[H^+]$ = 0.01 and 0.10 M, is accounted for by H^+-induced hydroxo-bridge cleavage leading to mononuclear products (en = ethylenediamine, trien = triethylenetetra-amine). Contrary to a previous report μ-peroxo-complexes remain less active than H_2O_2 with Fe^{2+} as reductant.

RELATIVELY few studies have been reported in which the ease of reduction of the peroxo-bridge in dicobalt(III) complexes has been assessed.[1,2] Recently McLendon and Martell [3] investigated, by the stopped-flow method, the Fe^{2+} reduction of four μ-hydroxy-μ-peroxo-complexes, including $[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$ (en = ethylenediamine) (rate constant 400 M^{-1} s^{-1} at 25 °C †). Rate constants reported are surprisingly large compared with those for the Fe^{2+} reduction of other μ-peroxo-complexes $[(en)_2Co(NH_2)(O_2)Co(en)_2]^{3+}$ (*ca.* 1.1 M^{-1} s^{-1}),[4] $[(trenen)Co(O_2)Co(trenen)]^{4+}$ (trenen = tetraethylenepenta-amine) ($<6.6 \times 10^{-4}$ M^{-1} s^{-1}),[4] and $[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+}$ (no apparent reaction of protonated form) [5] all of which are much less reactive than H_2O_2 (58 M^{-1} s^{-1}).[6] Because of this anomaly and the possible inter-dependence of redox and bridge-cleavage processes, we have briefly re-investigated the reported redox reactivity with Fe^{2+} and examined the H^+-induced decomposition of two μ-hydroxo-μ-peroxo-complexes $[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$ and $[(trien)Co(OH)(O_2)Co(trien)]^{3+}$ (trien = triethylenetetra-amine).

EXPERIMENTAL

Preparation of the μ-hydroxo-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] perchlorate, $[(en)_2Co(OH)(O_2)Co(en)_2][ClO_4]_3\cdot H_2O$,[6] complex was as follows. The compound $Co[ClO_4]_2\cdot 6H_2O$ (3.69 g, G. F. Smith), and ethylenediamine (1.5 g, B.D.H. Lab. Reagent) were dissolved in 1 : 1 ethanol–water (50 ml). The solution was cooled, filtered, and a brisk stream of oxygen passed through the filtrate for 3 min. Sodium perchlorate, $Na[ClO_4]\cdot H_2O$ (40 g, B.D.H. AnalaR), was added and the solution stirred with ice cooling for *ca.* 1 h. The brown solid obtained was filtered off, washed with ethanol and diethyl ether, and air dried. Yield: 1.3 g. The spectrum in H_2O gave $\lambda_{max.}$ 355 nm (ε 5.38×10^3 M^{-1} cm^{-1}) in excellent agreement with literature values.[7]

To prepare the μ-hydroxo-μ-peroxo-bis[triethylenetetraaminecobalt(III)] complex, $[(trien)Co(OH)(O_2)Co(trien)][ClO_4]_3$ (a salt not previously reported), $Co[ClO_4]_2\cdot 6H_2O$ (3.6 g) and triethylenetetra-amine (1.8 g, R. N. Emanuel) were dissolved in water (50 ml). The solution was cooled, and a brisk stream of oxygen passed through. After filtering, $Na[ClO_4]\cdot H_2O$ (40 g) was added, followed by a large excess of ethanol (*ca.* 1 l). The walls of the beaker were scratched with a glass rod. The brown fluffy precipitate was filtered off on a sintered glass filter (no. 3 porosity), washed three times with ethanol (*N.B.* the solid was not allowed to suck dry except on the last washing), and transferred quickly to a desiccator, where it was stored *in vacuo* over silica gel. The spectrum in H_2O gave $\lambda_{max.}$ 355 nm (ε 4.7×10^3 M^{-1} cm^{-1}) in good agreement with a previous value for the thiocyanate salt [7] (Found: C, 19.0; H, 5.2; N, 14.4. Calc. for $C_{12}H_{37}Cl_3Co_2N_8O_{15}$: C, 19.0; H, 4.20; N, 14.8%).

Sodium perchlorate, perchloric acid, and potassium nitrate (B.D.H. AnalaR) were used. Iron(II) perchlorate (G. F. Smith) was made up in *ca.* 0.10 M $HClO_4$ under N_2 and standardised by titration with cerium(IV).

Decomposition (25 °C) of the μ-hydroxo-μ-peroxo-complexes (initially in H_2O–$Na[ClO_4]$) induced by mixing with a solution of $HClO_4$, final I = 0.20 M (H–$Na[ClO_4]$), was monitored at 355 nm using the stopped-flow technique. For the en complex first-order rate constants were obtained from the slope (× 2.303) of plots of absorbance log ($A_t - A_\infty$) against time. Such plots were linear for about three reaction half-lives.

RESULTS AND DISCUSSION

Whereas the H^+-induced decomposition of the en complex is reported to proceed according to (1),[8] and

$$Co^{III}\cdot O_2^{2-}\cdot Co^{III} \xrightarrow{H^+} 2Co^{II} + O_2 \qquad (1)$$

certainly at pH ⩾ 1.5 this represents the major reaction path, the alternative route (2) contributes as much as

$$Co^{III}\cdot O_2^{2-}\cdot Co^{III} \xrightarrow{H^+} 2Co^{III} + H_2O_2 \qquad (2)$$

50% to the decomposition of the trien complex, depending on pH (0.4—2.0) and the identity of anions present.[10] The *meso* and racemic forms of the en complex react

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† Throughout this Note: M = mol l^{-1}.

at different rates.[8] Oxygenation of solutions of Co^{II}-trien complex appear to yield preferentially three of the eight possible isomers.[8]

Rate constants, $k_{obs.}$, for the decomposition of the μ-hydroxo-μ-peroxo-complex $[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$ at 25 °C, $I = 0.20$ M ($Na[ClO_4]$) except as stated. Number of runs indicated in parentheses

$[H^+]$/M	$10^5[Co^{III}_2]$/M	$k_{obs.}/s^{-1}$
0.010	1.44	0.0188
0.010	1.44	0.0172 [a]
0.010	1.44	0.0184 [a,b]
0.020	1.44	0.033(2)
0.025	1.44	0.036(2)
0.050	1.44	0.056
0.050	3.50	0.049
0.050	7.50	0.054
0.075	1.44	0.071
0.075	1.44	0.081
0.10	1.44	0.075 [c]
0.10	1.44	0.086 [b]
0.10	1.44	0.089
0.10	1.44	0.095 [a]
0.10	1.44	0.094 [a,b]

[a] $I = 0.20$ M ($K[NO_3]$). [b] $[Fe^{2+}] = 1.0 \times 10^{-3}$ M. [c] $[Fe^{2+}] = 0.3 \times 10^{-3}$ M.

Only a single stage was observed in the decomposition of the en complex where, from earlier studies,[8] the perchlorate salt is believed to be predominantly in the *meso* form.* First-order rate constants $k_{obs.}$, Table, give a fit to (3) where the acid dissociation constant K_a

$$k_{obs.} = k[H^+]/([H^+] + K_a) \qquad (3)$$

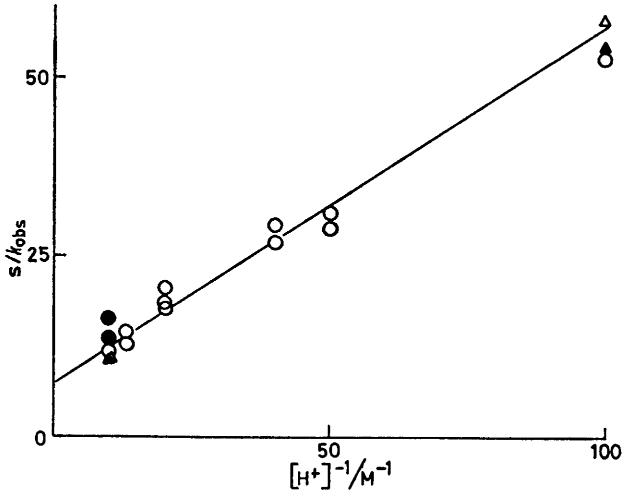
and rate constant k are as defined in equations (4) and (5) for a μ-hydroxo-μ-peroxo-complex E^{3+}. A plot of

$$EH^{4+} \underset{}{\overset{K_a}{\rightleftharpoons}} E^{3+} + H^+ \qquad (4)$$

$$EH^{4+} \xrightarrow{k} \text{products} \qquad (5)$$

$1/k_{obs.}$ against $[H^+]^{-1}$ is linear, see Figure. From a least-squares fit to (3) $K_a = 0.064 \pm 0.007$ M (pK_a 1.2) and $k = 0.133 \pm 0.012$ s^{-1} at 25 °C. The μ-hydroxo-μ-peroxo-complexes are stable to decomposition in H_2O–$Na[ClO_4]$ solutions prior to mixing with H^+ or H^+ and Fe^{2+}. Previously protonation of the μ-peroxo-bridge of $[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+}$ ($K_a = 0.084$ M at 25 °C) has been found to stabilize the complex to decomposition ($k = 84$ s^{-1}) yielding products as in (1).[5,11] Here protonation destabilizes the complex, presumably by protonation and cleavage of the hydroxo-bridge. An interesting feature is the close similarity of protonation constants observed for μ-hydroxo- and μ-peroxo-bridges in such dicobalt(III) complexes. The extent to which a second bridge stabilizes the μ-peroxo-complexes to decomposition by intramolecular electron transfers is also noted.

The perchlorate salt of the trien complex has been isolated as described. Acid-induced decomposition, $[H^+] = 0.10$ M, $I = 0.20$ M (H–$Na[ClO_4]$), gave at least three observable stages, the first requiring *ca.* 20 s and the last up to 20 min to proceed to completion. Rate constants were of the same magnitude as those reported in ref. 8. Our findings with both en and trien complexes are very similar therefore to those of Fallab and co-workers, although we have not attempted to confirm an assignment of concurrent (as opposed to consecutive †) reaction steps.



Plot of $(k_{obs.})^{-1}$ against $[H^+]^{-1}$ for the H^+-induced decomposition of $[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$ at 25 °C, $I = 0.20$ M ($Na[ClO_4]$) (○), and $I = 0.20$ M ($K[NO_3]$) (△). Runs with added $[Fe^{2+}] = (0.3 \text{ and } 1.0) \times 10^{-3}$ M are also marked (● and ▲ respectively)

When Fe^{2+} in the range $(0.3$—$1.0) \times 10^{-3}$ M was added at the same time as acid, $[H^+] = 0.01$ and 0.10 M for the en complex, $[H^+] = 0.10$ M for the trien one, no difference in rate of loss of μ-peroxo-absorbance at λ = 355 nm was observed. Moreover with each complex, decomposition is at the same rate in $I = 0.20$ M (H–$K[NO_3]$) (the conditions used in ref. 3) with and without added Fe^{2+}. A rate constant of 400 M^{-1} s^{-1} reported[3] for the Fe^{2+} reduction of the en complex would give a first-order contribution of >0.12 s^{-1} under our conditions, which would be readily detected alongside the rate constant for decomposition, $k_{obs.} < 0.09$ s^{-1}. Similarly the rate constant reported for the Fe^{2+} reduction of the trien complex (25 M^{-1} s^{-1}),[3] giving a first-order contribution of 0.025 s^{-1} under our conditions, would have been detectable alongside the decomposition process, $k_{obs.}$ *ca.* 0.014 s^{-1} (first stage) or $k_{obs.}$ *ca.* 0.008 5 s^{-1} (second stage). The results obtained for the two complexes described would seem to exclude any possibility that different isomeric forms display radically different redox behaviour towards Fe^{2+}. It is possible that in the previous study by McLendon and Martell[3] the μ-hydroxo-μ-peroxo-decomposition process has been incorrectly assigned to a redox reaction with the Fe^{2+}. The data which they report for Fe^{2+} reduction of related μ-superoxo-complexes on the other hand seem perfectly

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* Results obtained by Professor Fallab's group at the University of Basel give $k \approx 0.46[H^+]/(0.032 + [H^+])$ for the *meso* form and $k \approx 0.16[H^+]/(0.065 + [H^+])$ for the racemate at 25 °C, $I = 1.0$ M (KCl).

† Decomposition in the presence of co-ordinating anions could yield intermediates with the anions co-ordinating at the time of the hydroxo-bridge cleavage. Contribution from consecutive reaction steps could then contribute.

acceptable in view of the recently reported μ-superoxo–μ-peroxo-reduction potentials.[12]

The prevailing pattern of redox behaviour remains therefore that the μ-peroxo-dicobalt(III) complexes are much less redox active with Fe^{2+} than is H_2O_2.

Two of us (N. A. S. and M. F.) are grateful for the Award Scholarships from the Kuwait Government and British Council respectively. It is a pleasure to acknowledge discussions and correspondence with Professor S. Fallab. We also thank Professor W. K. Wilmarth for communicating results to us prior to publication. This work was carried out at the University of Leeds.

[0/460 *Received, 25th March*, 1980]

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