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Formation of Hydrogen Peroxide by Two-stage Acid Hydrolysis of *trans*(NO_2,O_2)-[μ-Peroxo-bis{nitrtobis(ethylenediamine)-cobalt(III)}] and Reaction Kinetics

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The aquation rate of *trans*(NO_2,O_2)-$[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)]^{2+}$ has been measured in acidic aqueous solution at $[H^+]=0.003$—0.25 M and $I=0.50$ M ($LiClO_4$), the final products being *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ and H_2O_2 in marked contrast to the acid decomposition of $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ where the final products are Co(II) and O_2. The reaction consists of two stages, each of which has preequilibrium of protonation. The observed rate constants for the first and second stages are consistent with the formula, $k_i^{obsd}=k_iK_i[H^+]/(1+K_i[H^+])$ (i=1, 2), indicating the existence of protonated reactive forms in both stages. The rate constants, activation parameters and equilibrium constants are $k_1=7.46\ s^{-1}$ (25 °C), $\Delta H_1^{\ne}=66.9\pm1.3$ kJ mol^{-1}, $\Delta S_1^{\ne}=-2.9\pm4.2$ J K^{-1} mol^{-1}, and $K_1=3.44\ M^{-1}$ (25 °C) for the first stage and $k_2=0.400\ s^{-1}$ (25 °C), $\Delta H_2^{\ne}=85.4\pm2.1$ kJ mol^{-1}, $\Delta S_2^{\ne}=33.5\pm7.1$ J K^{-1} mol^{-1}, and $K_2=2.98\ M^{-1}$ (25 °C) for the second stage. The solution of the reaction intermediate $[Co(NO_2)(O_2H)(en)_2]^+$ has been obtained by ion exchange technique and characterized by the UV and visible spectra. The factors which decide the reaction path are discussed.

While μ-hyperoxo dicobalt(III) complexes are usually resistant to acids, the μ-peroxo dicobalt(III) complexes are more or less susceptible to them. Thus $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ is decomposed almost instantaneously in acidic solution to give Co^{2+}, NH_4^+, and O_2, the reaction rate, however, being inverse in $[H^+]$.[1,2] On the other hand, double-bridged μ-amido-μ-peroxo dicobalt(III) complexes do not evolve oxygen but undergo isomerization.[3] A third case would be formation of hydrogen peroxide and mononuclear cobalt(III) complexes, as exemplified by μ-peroxo cyano cobalt(III) complex.[4] The kinetic study of the third case has not yet been reported.

We are now going to report a new example of this third case, *i.e.*, the reaction of *trans*(NO_2,O_2)-[μ-peroxo-bis{nitrobis(ethylenediamine)cobalt(III)}] complex with acid. The reaction gives 2 mol of mononuclear cobalt(III) complex and 1 mol of hydrogen peroxide from 1 mol of the μ-peroxo dicobalt(III) complex. This very clear-cut stoichiometry enabled us to obtain the reaction rate and the acid association equilibrium constants on a quantitative basis.

Experimental

Preparation. trans-(NO_2,O_2)-[μ-*Peroxo-bis{nitrobis(ethylenediamine)cobalt(III)}] Perchlorate Dihydrate*: The perchlorate salt was prepared by the addition of sodium perchlorate to an aqueous solution of the corresponding nitrate.[5] Found: C, 13.21; H, 4.86; N, 19.35%. Calcd for $[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)](ClO_4)_2\cdot 2H_2O$: C, 13.40; H, 5.06; N, 19.53%.

trans-[*Aquanitrobis(ethylenediamine)cobalt(III)*] *Perchlorate Hydrate*: Sixty percent $HClO_4$ (10 ml) was added to the μ-peroxo complex (1 g, see above) and filtered. Ethanol (20 ml) was added slowly to the solution, which was then cooled for several hours. Orange crystals deposited were filtered and washed successively with ethanol and diethyl ether. Yield 0.9 g. Found: C, 10.45; H, 4.35; N, 15.42%. Calcd for $[Co(NO_2)(OH_2)(en)_2](ClO_4)_2\cdot H_2O$: C, 10.44; H, 4.38; N, 15.22%. The identification of the compound as the *trans* isomer has been made spectrophotometrically.[6] The *trans* configuration has also been confirmed by ir spectroscopy: one band (888 cm^{-1}) between 870 and 900 cm^{-1} [7] and three bands (600, 565, and 520 cm^{-1}) between 500 and 610 cm^{-1}.[8]

Analysis of the Reaction Products. *Hydrogen Peroxide*: The μ-peroxo complex $[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)](ClO_4)_2\cdot 2H_2O$ was dissolved in 1 M H_2SO_4 and the hydrogen peroxide formed was titrated with permanganate, using *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ solution as a reference. As expected from Eq. 1 in the following section, 0.99 ± 0.01 mol of H_2O_2 was formed for each mole of the μ-peroxo complex.

trans-[*Aquanitrobis(ethylenediamine)cobalt(III)*]$^{2+}$ *ion*: The μ-peroxo complex was dissolved in 0.1 M $HClO_4$ and the spectrum of *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ formed was taken. The ε-value (at $\lambda_{max}=335$ nm 1015 cm^{-1} M^{-1}) was in good agreement with the literature value.[6]

Measurement of Reaction Kinetics. A large excess of perchloric acid over the μ-peroxo complex was used in each run ($I=0.5$ M, $LiClO_4$). The reaction was pursued by the observation of absorption changes at 305 nm at which large differences can be found between absorptivities of the complexes present. As will be described in the following section, the reaction consists of two distinct stages, each stage showing strong acid dependence. In the region of lower acid concentration ($[H^+]$[9] ≈ 0.003—0.01 M, and [complex] ≈ 0.0001 M) at 15.4 °C, both stages were followed by the conventional spectrophotometric method using a Hitachi 200-10 Spectrophotometer. In the region of higher acid concentration ($[H^+]\approx 0.01$—0.25 M, and [complex] ≈ 0.001 M), the first stage of the reaction was followed by the stopped flow technique using Union RA 401 Instrument, while the second stage was monitored by the conventional technique.

Separation of the Intermediate. An attempt was made by use of ion exchange technique to isolate the intermediate produced at the first stage of the reaction. Thirty-six milligram (5×10^{-5} mol) of μ-peroxo complex perchlorate was dissolved in 20 ml of water, 1 ml of 0.1 M $HClO_4$ (10^{-4} mol) was added to it and the mixture was poured onto the top of a coloumn of 5 cm in length and 0.8 cm in diameter containing Dowex 50W-X2 cation exchange resin in Na-form. Elution with 0.5 M $NaClO_4$ gave a fraction of orange color, and successive elution with 1.0 M $NaClO_4$ containing 0.01 M $HClO_4$ gave another orange fraction which was spectrophotometrically identified[6] with *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$. The first eluate is considered to contain the desired intermediate having charge +1 as judged from its easier elution than in the case of *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$.

Results

Reaction Stoichiometry and Spectra of Related Complexes. Spectrophotometry as well as permanganate titration of the final reaction products proved formation of 2 mol of *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ and 1 mol of H_2O_2 from 1 mol of the dicobalt(III) complex, thus pointing to the following stoichiometry:

$$[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)]^{2+} + 2H^+ + 2H_2O \longrightarrow 2\,trans\text{-}[Co(NO_2)(OH_2)(en)_2]^{2+} + H_2O_2. \quad (1)$$

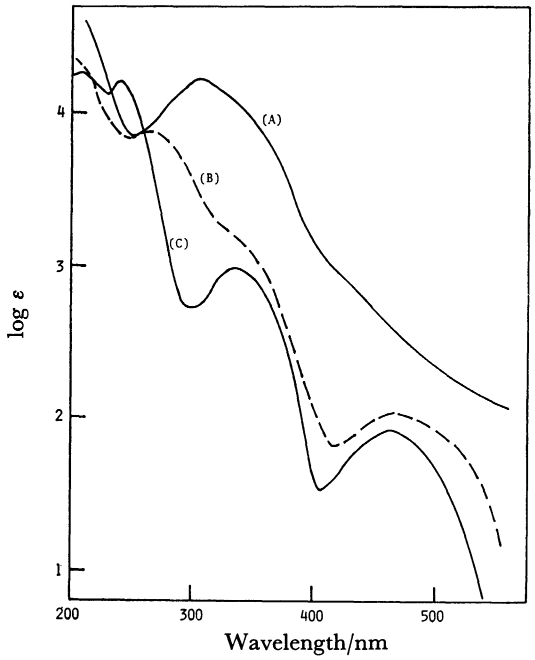


Fig. 1. UV and visible spectra.
(A): *trans*(NO_2,O_2)-$[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)]^{2+}$,
(B): *trans*-$[Co(NO_2)(O_2H)(en)_2]^{+}$,
(C): *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$.

Spectra of the starting material and the final product are given by curves A and C in Fig. 1, respectively. Peak positions and ε-values (in parentheses) are as follows: $[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)](ClO_4)_2\cdot 2H_2O$, 307 nm (16000); *trans*-$[Co(NO_2)(OH_2)(en)_2](ClO_4)_2\cdot H_2O$, 205 (17700), 238 (15200), 335 (975), and 463 nm (86). The ε-value (975) of the latter at 335 nm is slightly (*ca.* 4%) different from that (1015) obtained directly from the acid hydrolysis of μ-peroxo dicobalt(III) complex. This could be explained by assuming *trans* to *cis* isomerization (*ca.* 3%) during the course of the formation reaction.[10] Although the isolation of the intermediate as crystals has not yet been succesful, its absorption spectrum (Fig. 1, curve B) has been obtained.[11] The absolute ε-values of the spectrum were calculated in reference to the ε-values of *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ produced therefrom by further action of perchloric acid.

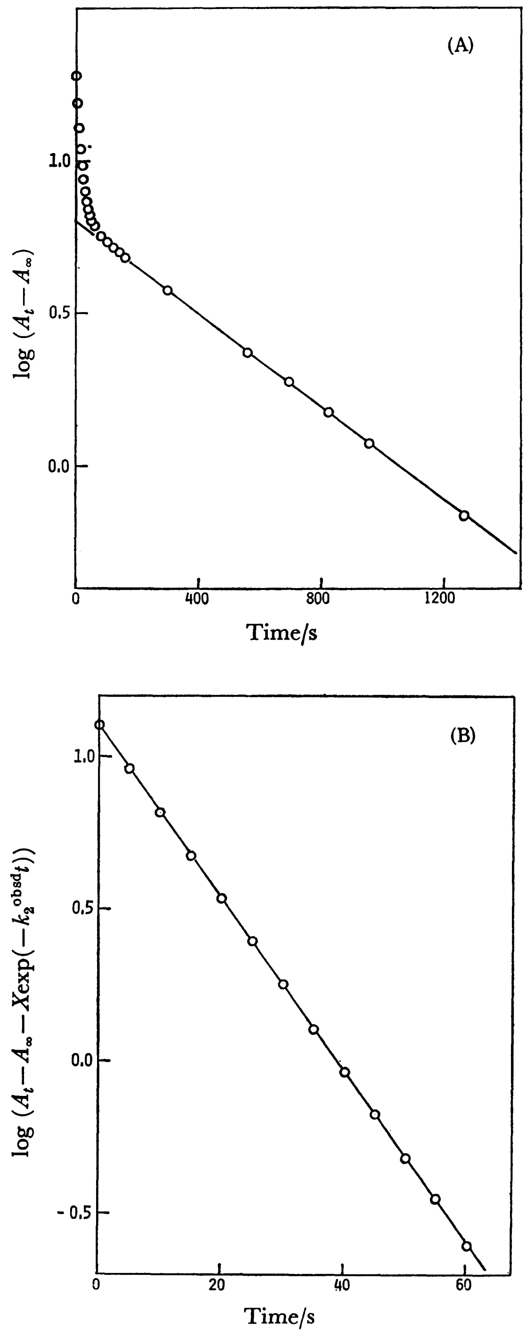


Fig. 2. Analysis of the consecutive reactions at 15.4 °C, $I=0.5$ M ($LiClO_4$), $[H^+]=5.69\times10^{-3}$ M, [complex]$\approx 1\times10^{-4}$ M.
(A) Plot of log $(A_t - A_\infty)$ *vs.* time for the second stage.
(B) Plot of log $(A_t - A_\infty - X\exp(-k_2^{obsd}t))$ *vs.* time for the first stage, where $X=6.52$ and $k_2^{obsd}=1.75\times10^{-3}$ s^{-1} obtained from (A) were used.

Kinetic Data. As is seen in Fig. 2(A), the reaction consists of two stages having considerably different rate, both of which are strongly acid dependent. Since the first stage dies down very quickly, the plot $\log(A_t - A_\infty)$ *vs.* t except at the initial stage forms a good straight line, from which the pseudo-first order rate constant of the second stage k_2^{obsd} can be obtained. The pseudo-first order rate constant of the first stage can then be obtained by re-plotting $\log(A_t - A_\infty - X\exp(-k_2^{obsd}t))$ *vs.* t (Fig. 2(B)), where $\log(X)$ is the intercept of the first plot

(Fig. 2(A)).[12] In the actual case, k_2^{obsd} is small enough as compared with k_1^{obsd} and the term $X\exp(-k_2^{\text{obsd}}t)$ may be regarded as nearly constant in the time scale used in the estimation of k_1^{obsd}. This approximation was used in most of the present treatment since such a treatment proved to give the same result as when the exact consecutive treatment was applied.

TABLE 1. FIRST ORDER RATE CONSTANTS, $k_1^{\text{obsd}}/\text{s}^{-1}$ FOR THE ACID HYDROLYSIS OF *trans*(NO_2,O_2)-[μ-PEROXO-BIS{NITROBIS(ETHYLENEDIAMINE)COBALT(III)}] TO THE INTERMEDIATE, AND $k_2^{\text{obsd}}/\text{s}^{-1}$ FOR THE ACID HYDROLYSIS OF THE INTERMEDIATE TO THE FINAL PRODUCTS; $I=0.5$ M ($LiClO_4$), $\lambda=305$ nm[a)]

$[H^+]$/M	Temp/°C				
	10.8	15.6	20.0	25.0	30.1
(A) $k_1^{\text{obsd}}/\text{s}^{-1}$					
0.030	0.201	—	—	—	1.01
0.050	0.328	0.512	0.753	1.11	1.59
0.100	0.541	0.862	1.30	1.87	2.77
0.150	0.705	1.15	1.70	2.52	3.83
0.200	0.830	1.38	2.05	3.06	4.77
0.250	0.948	1.59	2.30	3.55	5.31

$[H^+]$/M	Temp/°C				
	5.0	10.2	15.4	20.2	25.0
(B) $k_2^{\text{obsd}}\times 10^2/\text{s}^{-1}$					
0.0147	—	—	—	0.811	—
0.0294	0.267	—	—	—	2.73
0.0493	0.426	0.794	1.35	2.55	4.45
0.0985	0.769	1.40	2.41	4.48	7.85
0.148	1.01	1.87	3.27	6.09	10.3
0.198	1.18	2.23	3.87	7.27	12.4
0.247	1.32	2.49	4.45	8.49	14.5

a) Experiments at lower $[H^+]$ were made only at 15.4 °C:

$[H^+]\times 10^3$/M	$k_1^{\text{obsd}}\times 10^2/\text{s}^{-1}$	$k_2^{\text{obsd}}\times 10^4/\text{s}^{-1}$
2.72	2.94	8.25
5.69	6.40	17.5
8.65	9.77	27.2
11.6	13.1	37.2

These data were not used in the estimation of k_1 and k_2 in Table 2.

Both rate constants k_i^{obsd} (i=1, 2) obtained in this way increased with the increase in acidity with a certain tendency of saturation (Table 1), implying the existence of preequilibrium of protonation in both stages. Linear dependence of $1/k_i^{\text{obsd}}$ (i=1, 2) against $1/[H^+]$ was observed at each temperature as consistent with (2) for both stages as can be seen in Figs. 3(A) and 3(B), and from these we could calculate the values of k_1, K_1, k_2, and K_2, *i.e.*, the rate and preequilibrium constants for the first and second stages, respectively (Table 2).

$$k_i^{\text{obsd}} = k_i K_i [H^+]/(1+K_i[H^+]). \qquad (2)$$

The relevant activation and thermodynamic parameters are given in Table 3.

The Nature of the Reaction Intermediate and the Constituion of the Reaction. On addition of perchloric acid to the solution of the intermediate as described in Experimental, spectral change was observed with isosbestic points as shown in Fig. 4, and the final solution was found to contain *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ and H_2O_2 as evidenced by spectrophotometry and permanganate titration. These findings and estimated charge +1 suggest that the intermediate would be *trans*-$[Co(NO_2)(O_2H)(en)_2]^+$ produced from the pro-

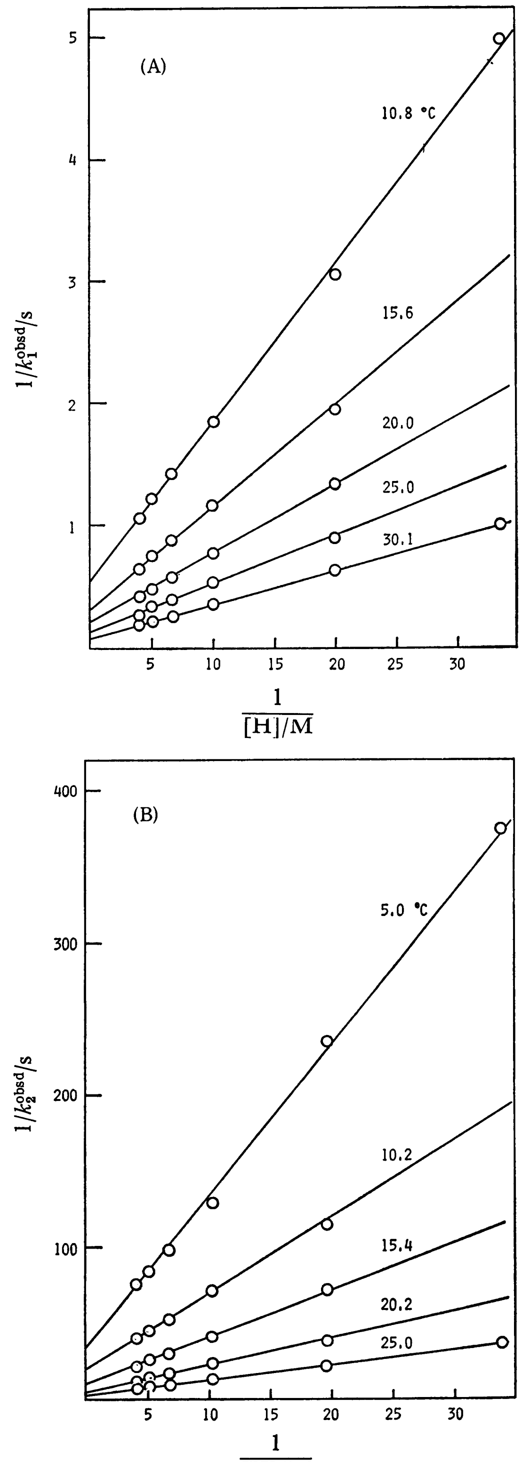


Fig. 3. Plot of $1/k_i^{\text{obsd}}$ *vs.* $1/[H^+]$ for the acid hydrolysis of the μ-peroxo complex $[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)]^{2+}$, at $I=0.5$ M ($LiClO_4$).
(A): First stage, (B): second stage.

Table 2. Values of k_i and K_i (i=1,2) obtained from the fit of the data in Table 1 to the Eq. 2; I=0.5 M ($LiClO_4$)

	Temp/°C	k_1/s^{-1}	K_1/M^{-1}
(A)	10.8	1.92	3.95
	15.6	3.16	3.84
	20.0	4.70	3.81
	25.0	7.46	3.44
	30.1	12.9	2.82
	Temp/°C	**k_2/s^{-1}**	**K_2/M^{-1}**
(B)	5.0	0.0307	3.22
	10.2	0.0596	3.05
	15.4	0.106	2.98
	20.2	0.208	2.77
	25.0	0.400	2.98

Table 3.

Activation parameters relevant to k_1 and k_2. I=0.5 M ($LiClO_4$).

(A) $\Delta H_1^{\ddagger}=66.9\pm1.3$ kJ mol^{-1}

$\Delta S_1^{\ddagger}=-2.9\pm4.2$ J K^{-1} mol^{-1}

(B) $\Delta H_2^{\ddagger}=85.4\pm2.1$ kJ mol^{-1}

$\Delta S_2^{\ddagger}=33.5\pm7.1$ J K^{-1} mol^{-1}

Thermodynamic parameters relevant to K_1 and K_2.

(A) $\Delta H_1=-11.7\pm2.1$ kJ mol^{-1}

$\Delta S_1=-28.9\pm22.6$ J K^{-1} mol^{-1}

(B) $\Delta H_2=-3.8\pm1.3$ kJ mol^{-1}

$\Delta S_2=-4.2\pm12.1$ J K^{-1} mol^{-1}

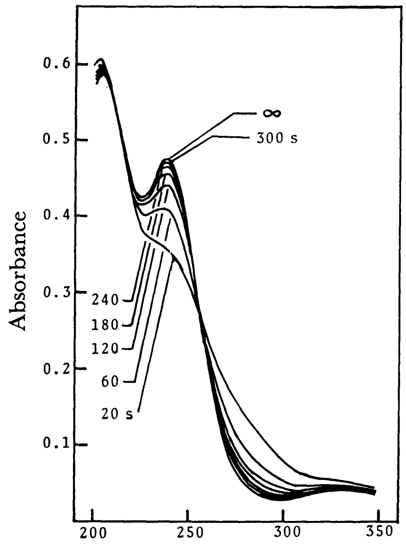


Fig. 4. Absorption changes for the acid hydrolysis of the intermediate *trans*-$[Co(NO_2)(O_2H)(en)_2]^+$ at 15 °C, I=0.5 M ($LiClO_4$), $[H^+]=0.0294$ M, and [complex]= 3.0×10^{-5} M.

tonated form of the starting complex *via* protonation preequilibrium,

$$[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)]^{2+} + H^+ \overset{K_1}{\rightleftharpoons} [(NO_2)(en)_2Co(O_2H)Co(en)_2(NO_2)]^{3+} \quad \text{(3-a)}$$

$$[(NO_2)(en)_2Co(O_2H)Co(en)_2(NO_2)]^{3+} + H_2O \xrightarrow{k_1} trans\text{-}[Co(NO_2)(O_2H)(en)_2]^+ + trans\text{-}[Co(NO_2)(OH_2)(en)_2]^{2+} \quad \text{(3-b)}$$

in conformity with the form of the rate equation. The second stage would then be the acid hydrolysis of the hydroperoxo intermediate into *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ and H_2O_2, being, again, initiated by protonation:

$$trans\text{-}[Co(NO_2)(O_2H)(en)_2]^+ + H^+ \overset{K_2}{\rightleftharpoons} trans\text{-}[Co(NO_2)(O_2H_2)(en)_2]^{2+} \quad \text{(3-c)}$$

$$trans\text{-}[Co(NO_2)(O_2H_2)(en)_2]^{2+} + H_2O \xrightarrow{k_2} trans\text{-}[Co(NO_2)(OH_2)(en)_2]^{2+} + H_2O_2. \quad \text{(3-d)}$$

The rate of acid hydrolysis of the intermediate in the solution separated by ion exchange technique ($k^{\rm obsd}=2.38\times10^{-2}$ s^{-1}, $[H^+]=0.0985$ M, 15.4 °C) was in good agreement with the acid hydrolysis rate of the second stage ($k_2^{\rm obsd}=2.41\times10^{-2}$ s^{-1}, $[H^+]=0.0985$ M, 15.4 °C).

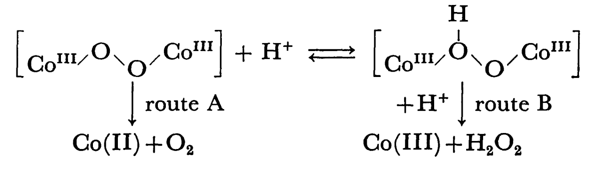
The *trans* structure of the starting μ-peroxo complex has already been established,[13] and *cis-trans* isomerization of $[Co(NO_2)(OH_2)(en)_2]^{2+}$ need not be considered here because of its slow isomerization rate.[6]

If the acid hydrolysis of the μ-peroxo compound is carried out under the exposure to sunlight, the absorbance at 335 nm of the final products decreases to *ca.* two thirds compared to the case without the sunlight exposure, indicating the appearance of an additional reaction path leading to Co(II) species. An attempt was made to find the wavelength most effective to bring about the side reaction using monochromated light from as apectrophotometer, but the intensity of the light from the spectrophotometer was found too weak to induce the side reaction.

If small amounts of acid were used for the separation of the intermediate, a different intermediate showed up, which had peaks at 337 and 462 nm and which did not give the *trans*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ even by the addition of excess amount of acids. The final products, in this case, have not yet been fully characterized.

Discussion

As stated in the introduction, the action of acid upon the μ-peroxo dicobalt(III) complexes causes in some cases the decomposition to Co(II) and O_2 (route A), and in other cases the hydrolysis to Co(III) complex and H_2O_2 (route B).



$$\begin{tikzcd}
\left[Co^{III}\diagup^{O}\diagdown_{O}\diagup Co^{III}\right] + H^+ \arrow[r, shift left] \arrow[d, "\text{route A}"] & \left[Co^{III}\diagup\overset{\overset{H}{|}}{O}\diagdown_{O}\diagup Co^{III}\right] \arrow[l, shift left] \arrow[d, "+H^+"', "\text{route B}"] \\
Co(II)+O_2 & Co(III)+H_2O_2
\end{tikzcd}$$

The main factors to decide the choice among these rather different modes, *i.e.*, route A and route B, appear to be the relative stability of Co(II) and Co(III) species and the ease with which the peroxo bridge is replaced.

The first group usually contains μ-peroxo single-bridged complexes only with amine ligands. The easiness in the decomposition of these complexes, as contrasted to the stability generally seen in mononuclear Co(III) complexes towards acids, probably owes its origin to the reducing power of O_2^{2-} which itself is liable to change to O_2 by the loss of electrons, and to the more labile nature of the μ-peroxo dicobalt(III) complexes[14] as compared with other cobalt(III) complexes, because of the presence of excess electrons in the antibonding π-orbitals of O_2. The addition of acid would reduce the concentration of NH_3 in solution by the formation of NH_4^+ and promotes replacement of NH_3 by H_2O in the coordination sphere of these rather labile complexes. This makes Co(III) unstable enough to be reduced by the binding O_2^{2-} group, resulting in the formation of Co(II) and O_2. In this case, protonation to O_2 bridge itself would be rather to pull electron pair from cobalt to O_2 bridge and hinder the liberation of O_2 as proved by the experiment by Ferrer *et al.*[2] who showed that in the acid decomposition of $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$, the protonated species is non-reactive.

In the acid hydrolysis of $[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)]^{2+}$, and possibly of $[Co_2O_2(CN)_{10}]^{6-}$ and $Co_2O_2(CN)_8(en)_2]^{2-}$, on the other hand, the protonated species is reactive and the final products are Co(III) and H_2O_2 (route B). The presence of electron-withdrawing CN^- or NO_2^- group in the coordination sphere would partly cancel the above-mentioned labilizing effect of O_2^{2-} in the μ-peroxo dicobalt(III) complexes which would otherwise cause the complex to choose the route A. The stronger ligand field of these ligands at the same time is considered to stabilize Co(III) which is the product of route B.

Relatively fast acid hydrolysis of *trans*-$[Co^{III}LCl(en)_2]^{n+}$ was reported in the case of $L=NO_2^-$ or CN^- as compared to the case of $L=NH_3$, and was explained in terms of the role of π-bonding: the electron-accepting group such as nitro and cyano reduce the electron density around the group trans to the nitro or cyano group and make it easier for a solvent molecule to attach itself to cobalt and to initiate the substitution.[15]

The NO_2^- coordinated in the *trans*-position to μ-peroxo bridge in the dicobalt(III) complexes thus seems to prepare an ideal situation for the complex to be hydrolyzed to form mononuclear Co(III) complex and H_2O_2 through route B.

The acid association constants K_1 (3.44 M^{-1}, 25 °C) and K_2 (2.98 M^{-1}, 25 °C) are similar to each other and also to the acid association constants of $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ (11.9 M^{-1}, 25 °C, $I=0.1$ M, as calculated from acid dissociation constant),[2] and $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(en)_2]^{3+}$ (5.1 M^{-1}, 25 °C, $I=0.1$ M).[3] μ-Peroxo dicobalt complexes thus have considerably greater tendency tc be protonated than hydrogen peroxide which is reported to have the acid association constant of $K \approx 10^{-3}$.[16]

Ferrer *et al.*[2] reported a relatively large entropy of activation (36.4 J K^{-1} mol^{-1}) in the acid decomposition of $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ through route A, and attributed it to the charge neutralization within the complex. Smaller value of entropy of activation ($\Delta S_1^{\ddagger}=-2.9$ J K^{-1} mol^{-1}) may be due to the difference in the reaction route. Entropy of activation of the second stage ($\Delta S_2^{\ddagger}=33.5$ J K^{-1} mol^{-1}), however, is not small and the situation seems to be too complicated to allow detailed discussions.

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9) Hydrogen ion concentrations were determined by titration with standard alkaline solution.

10) *cis*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$ has peaks at 329 nm ($\varepsilon=2100$).[6]

11) Peak positions and ε-values (in parentheses) are as follows: 205 (21700), 265 (7660), 350 (1180), and 467 nm (108 M^{-1} cm^{-1}). The hydrogen peroxide anion (HO_2^-) appeares to give a slightly weaker ligand field than water does.

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