Acid–Base Effects in the μ-Amido-μ-peroxobis(bisethylenediaminecobalt) Complex System

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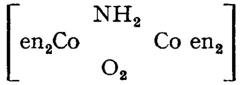
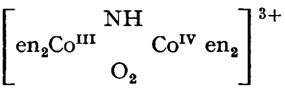
RATE studies by optical absorption spectroscopy have unveiled new features pertaining to a series of μ-amido-μ-peroxobis(bisethylenediaminecobalt) complexes, as summarized in Table 1. Here C′ and AH′ are the well-known green and red ions first considered as being isomeric[1] and later reported[2] to be paramagnetic and acid diamagnetic complexes, respectively; B′ is the normal diamagnetic ion newly obtained in an analysable salt,  $\left[\mathrm{en_2Co}\begin{matrix}\mathrm{NH_2}\\ \\ \mathrm{O_2}\end{matrix}\mathrm{Co\,en_2}\right](\mathrm{NO_3})_3,2\tfrac{1}{2}\mathrm{H_2O}$, and is probably the same as the one previously given[1] the formula  $\left[\mathrm{en_2Co^{III}}\begin{matrix}\mathrm{NH}\\ \\ \mathrm{O_2}\end{matrix}\mathrm{Co^{IV}\,en_2}\right]^{3+}$ The ion A′ appears only in definitely alkaline solution.

Thus, as indicated in the reaction scheme (Table 1), AH′ dissolved in water transforms to BH′ with rate constant k_{-2}. Since BH′ is a strong acid ($\mathrm{p}K_1 \sim 1$), it dissociates to B′ and H with no appreciable reverse reaction BH′ → AH′. For our experimental conditions ($[\mathrm{AH'}] \sim 10^{-3}$M), the reaction rate is described by the first-order rate constant k_{-2} to within a deviation of *ca.* 1%. Table 2 lists values of k_{-2} experimentally obtained, for water as well as $\mathrm{NaClO_4}$ solutions, in this approximation.

The rate constant k_{ox} for oxidation of AH′ by $\mathrm{(NH_4)_2Ce(NO_3)_6}$ in dilute $\mathrm{HClO_4}$ obtained from the optical studies was found (Table 2) to coincide with k_{-2} within experimental error at every temperature (5—25°), indicating that the conversion AH′ → BH′ is the rate-determining step in the oxidation of AH′ to C′; k_{ox} was not found to depend on the concentration of ceric ions or protons. The rate of increase of the e.s.r. signal[3] of the paramagnetic C′ formed was measured at a few temperatures and was found to be the same as the rate determined by the optical measurements. It was not possible to decide which of BH′ and B′ (or both) is directly oxidized, because their mutual equilibrium is established too quickly.

When a solution of B′ is acidified with sufficient $\mathrm{HClO_4}$ that [H] may be regarded as constant (*i.e.*,

TABLE 1

Reaction scheme of μ-amido-μ-peroxobis(bisethylenediaminecobalt) ions

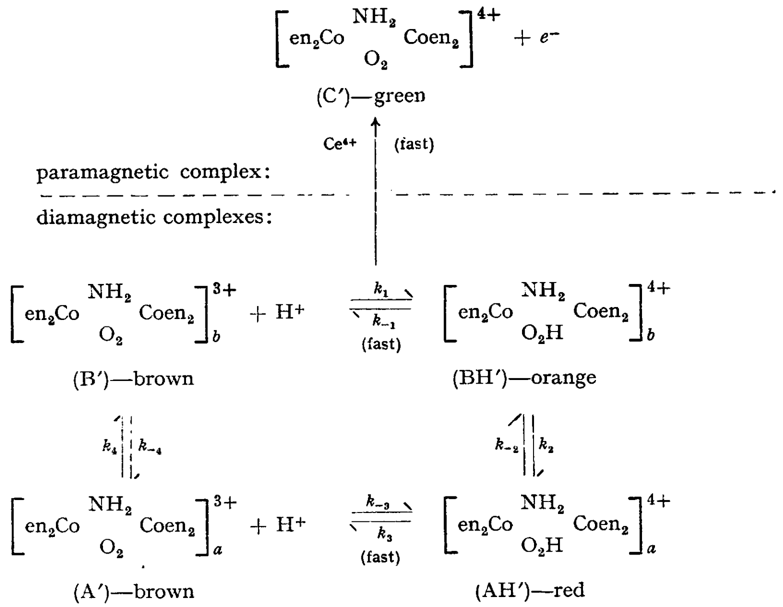


TABLE 2

Rate constants of isomerization and of oxidation of AH′

Temperature (°C)	k_{-2}(sec.$^{-1}$)* in water	in 0·106M-NaClO$_4$ aq.	in 0·265M-NaClO$_4$ aq.	k_{ox}(sec.$^{-1}$)†
$4{\cdot}9_3$	0·00430	—	0·00429	0·00436
$9{\cdot}9_2$	0·00827	0·00825	0·00825	0·00821
$14{\cdot}8_5$	0·0154	0·0153	0·01575	0·0157
$19{\cdot}9_3$	0·0293	0·0293	0·0296	0·0294
$24{\cdot}9_2$	0·0523	0·0523	0·0529	0·0525

* From absorbance change at 435 mμ: $\epsilon_{B'} = 830$, $\epsilon_{BH'} = 250$, $\epsilon_{AH'} = 110$.

† From absorbance change at 687 mμ: $\epsilon_{C'} = 400$, $\epsilon_{AH'} \sim 10 \gg \epsilon(Co^{IV})$

[H]/[B′] > 50), the mixture of B′ and BH′ immediately formed is transformed into an equilibrium mixture of B′, BH′, and AH′ with a pseudo-first-order rate constant

$$k_a = k_{-2} + k_2\,[H]/([H] + K_1).$$

Table 3 gives values of K_1, measured from the limiting molar extinction $\bar{\epsilon}_0 = (K_1\epsilon_{B'} + [H]\epsilon_{BH'})/(K_1 + [H])$ obtained by extrapolation to the time of dissolution of B′, and values of k_2 derived from the acid-dependence of k_a (using k_{-2} from Table 2). Details of the experiments, as well as derivation of the relevant rate equations, will be included in a paper to be published elsewhere.

The Arrhenius energy of activation and entropy of activation were calculated for the reaction AH′ → BH′ as $(E_{act})_{-2} = 20{\cdot}7 \pm 0{\cdot}2$ kcal./mole, $\Delta S^{\ddagger}_{-2} = 3 \pm 1$ e.u. and for BH′ → AH′ as $(E_{act})_2 = 15{\cdot}9 \pm 0{\cdot}4$ kcal./mole, $\Delta S^{\ddagger}_2 = -13 \pm 3$ e.u. The frequency factors ν (in sec.$^{-1}$) for these reactions were found to be given by $\log_{10} \nu = 13{\cdot}9 \pm 0{\cdot}1$ and $10{\cdot}4 \pm 0{\cdot}3$, respectively.

Although elemental analyses and the constancy of k_2 and k_{-2} with respect to ionic strength (Tables 2 and 3) suggests an isomeric relationship between the protonated diamagnetic complexes BH′ and AH′, the exact nature of the difference between these (and, analogously, B′ and A′) is as

TABLE 3

k_2 *and* pK_1 *obtained from acid-dependence of* k_a *and* $\bar{\epsilon}_0$ *at 435 m*μ

Ionic strength:	0·102		0·245	
Temp. (°c)	k_2(sec.$^{-1}$)	pK_1	k_2(sec.$^{-1}$)	pK_1
10	0·014	0·85	0·014	1·05
15	0·020	0·79	0·022	0·98
20	—	—	0·037	0·90
25	0·059	0·71	0·058	0·85

yet unknown. It seems possible that the isomerism results from occurrence of two different conformations of the peroxo-bridge.

Preliminary rate studies in basic solutions have shown that ion A′ has much higher extinction coefficient in most of the visible region and that $k_4 \sim 0{\cdot}1$ sec.$^{-1}$ and p$K_3 = -\log (k_3/k_{-3}) \sim 11$ at 10°.

The corresponding ammine complex ions (B, BH, AH and A) have shown parallel relationships, but determination of rate constants is more difficult because most of these ammine complexes are less stable than the ethylenediamine compounds.

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[1] A. Werner and A. Grun, *Annalen*, 1910, **375**, 61. In our work, the primes denote complexes with ethylenediamine ligands, with unprimed symbols reserved for analogous NH_3 complexes.

[2] L. R. Thompson and W. K. Wilmarth, *J. Phys. Chem.*, 1952, **56**, 5.

[3] E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, 1959, **63**, 1890.