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Reaction of Cobaloxime(II) with Hydroxide Ions

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The chemistry and catalytic properties of bis(dimethylglyoximato)cobalt(II) derivatives have been extensively studied from various aspects. In addition to being chemical analogues of vitamin B_{12r} [1, 2], these compounds activate molecular hydrogen [2–5, 7] and oxygen [8] and catalyze the hydrogenation [4, 6] and oxidation [9] of certain substrates.

One of the features of the cobaloxime(II) family that is still incompletely understood is the nature of interactions between cobaloxime(II) and hydroxide ions. Early studies by Schrauzer *et al.* [1] indicated a relatively slow reaction with strong base, which has been attributed to a disproportionation process:

$$2Co^{II}(Hdmg)_2 \xrightarrow{OH^-} Co^{I}(Hdmg)_2^- + Co^{III}(Hdmg)_2OH \qquad (1)$$

where Hdmg is the monoanion of dimethylglyoxime.

As no detailed investigations have been carried out on the kinetics of this reaction, we intended to perform a kinetic analysis of the disproportionation process. The results, as outlined in this contribution, are inconsistent with reaction (1) and require a new interpretation of the interaction of cobaloxime(II) with hydroxide ions [10].

Experimental

$Co(Hdmg)_2$ was prepared *in situ* by mixing methanolic solutions of $Co(ClO_4)_2\cdot 6H_2O$ and dimethylglyoxime under strictly anaerobic conditions. The vessel used for mixing the components permitted (*i*) the addition of methanolic NaOH to the $Co(Hdmg)_2$ prepared and (*ii*) transfer of the solution into a spectrophotometric cell under argon atmosphere. A Beckman ACTA MIV spectrophotometer was used to record the uv-vis spectra and to follow the reaction of $Co(Hdmg)_2$ with NaOH. Analytical grade chemicals were used throughout.

Results and Discussion

Figure 1 shows the spectral changes occurring in the visible range upon mixing 4 × 10^{-3} *M* $Co(Hdmg)_2$

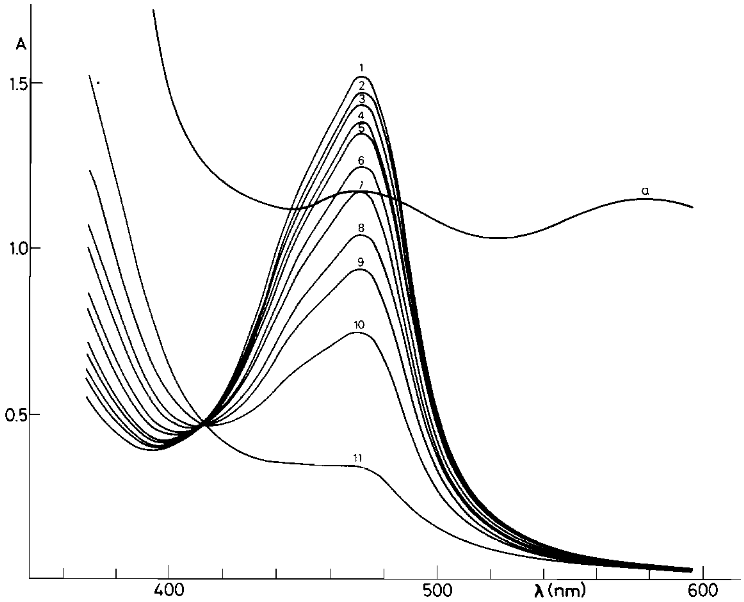


Fig. 1. Successive spectra of a solution containing 4 × 10^{-3} *M* $Co(Hdmg)_2$ and 20 × 10^{-3} *M* NaOH recorded 4.0 (1), 7.5 (2), 12.5 (3), 18 (4), 22 (5), 33 (6), 48 (7), 60 (8), 76 (9), 134 (10) min and 12 h (11) after mixing the reactants [curves numbered from top (1) to bottom (11)]. T = 25 °C. For comparison, the spectrum of 4 × 10^{-3} *M* $Co(Hdmg)_2^-$ is also shown (a).

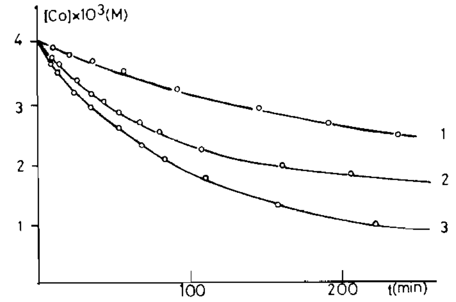


Fig. 2. Decrease of $Co(Hdmg)_2$ concentration with time; $[Co(Hdmg)_2]_o$ = 4 × 10^{-3} *M*: curve 1, 12 × 10^{-3} *M* NaOH; cuve 2, 20 × 10^{-3} *M* NaOH; curve 3, 24 × 10^{-3} *M* NaOH. Open circles are experimental points; Full line has been calculated using the average value of k_{obs}.

with 20 × 10^{-3} *M* NaOH in methanol under Ar. The process characterized by the successive spectra spans a time interval of about 12 hrs. The presence of two isosbestic points indicates the transformation of one set of reactants to one set of products. This would, in principle, be consistent with reaction (1). However, the disproportionation of $Co(Hdmg)_2$ should afford the cobaloxime(I) species $Co^I(Hdmg)_2^-$, which is known to absorb strongly in the 500–700 nm range. For comparison, Fig. 1 shows also the spectrum of 4 × 10^{-3} *M* $Co^I(Hdmg)_2^-$, which has been prepared by reducing 4 × 10^{-3} *M* $Co(Hdmg)_2$ with excess $NaBH_4$. This amount of $Co^I(Hdmg)_2$ would be expected to form if eqn. (1) correctly represented the reaction in question. (The other disproportionation product, $Co^{III}(Hdmg)_2OH$, does not absorb appreciably above 500 nm.)

The lack of absorption in the 500–700 nm range precludes that $Co^I(Hdmg)_2$ is a product of the reaction of $Co(Hdmg)_2$ with NaOH. Consequently, the spectral changes observed upon mixing with NaOH are *not* due to disproportionation as given by eqn. (1), and a completely different interpretation is necessary.

The kinetics of the reaction were followed spectrophotometrically at 470 nm. Figure 2 shows the decrease in absorbance with time. The analysis of the kinetic curves reveals that the disappearance of $Co(Hdmg)_2$ obeys the rate law

$$-\frac{d[Co]}{dt} = k_{obs}[Co]([OH^-]_o - [Co]_o + [Co])^2$$

In other words, the reaction is first order with respect to cobaloxime(II) and second order with respect to OH^- concentration [Co is $Co(Hdmg)_2$ and subscript 'o' refers to initial concentrations]. Upon integration, the above kinetic equation leads to

TABLE I. $Co_o = 4 \times 10^{-3}$ *M*; $[OH^-]_o = 20 \times 10^{-3}$ *M*; T = 25 °C.

t (min)	k_{obs} (calc)*
2.5	17.9
6	18.1
13	16.8
22.5	16.8
33	16.8
42	16.8
51	16.8
60	16.9
80	16.8
140	15.2

*Average value 16.9 ± 0.4.

TABLE II. Observed Rate Constants at T = 25 °C.

$[Co]_o \times 10^3$ (*M*)	$[OH^-]_o \times 10^3$ (*M*)	k_{obs} (M^{-2} min^{-1}) (average of 3 runs)
4	24	17.1 ± 0.5
4	20	16.8 ± 0.5
4	12	15.6 ± 0.5
4	4	16.5 ± 0.5
6	20	15.9 ± 0.5
2	20	17.0 ± 0.5
3	20	16.6 ± 0.5

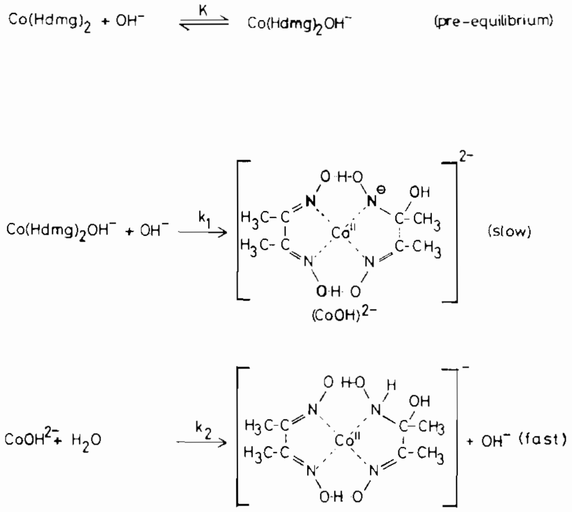
$$k_{obs}t = \frac{1}{Q^2} \times \ln\frac{([Co] + Q)[Co]_o}{[Co][OH^-]_o} + \frac{[Co]}{[Co] + Q} + \frac{[Co]_o}{[OH^-]_o}$$

where $Q = [OH^-]_o - [Co]_o$.

The validity of the above kinetic law is illustrated by the data in Tables I and II. The values of k_{obs} calculated for various points of a given run (Table I) are in very good agreement up to about 85% reaction. Good agreement is also found between k_{obs} values determined from kinetic measurements at different initial concentrations (Table II).

Numerical integration by the Runge-Kutta method, using the rate constant obtained form the above procedure reproduces the experimental kinetic curves with fair accuracy (full lines in Fig. 2).

The experimental data concerning the relatively slow reaction of $Co(Hdmg)_2$ with OH^- ions indicate that we are observing a phenomenon analogous to that described by Gillard *et al.* [2], referred to also as "covalent hydration". According to his studies, Pt(II), Pd(II), Fe(II) and Ru(II) complexes of 2,2-bipyridine and 1,10-phenanthroline undergo hydration and methanolation or ethanolation at one or more of the >C=N– bonds of the ligand. By analogy, we assume that a similar hydration process may take place also at the >C=N– bonds of coordinated dimethylglyoxime. Along these lines, we propose that the observed slow process is the covalent hydration of $Hdmg^-$, catalyzed by OH^- ions, depicted by the following steps:



This Scheme implies that only the OH^- derivative formed in the pre-equilibrium step is capable of covalent hydration. The contribution of $Co(Hdmg)_2$, *i.e.* a possible first order term in OH^- seems to be negligible under the conditions used. It should be noted that equilibrium K is shifted to the left as no absorbance jump is observed upon mixing the cobaloxime(II) solution with excess OH^-. In terms of the above scheme, $k_{obs} = Kk_1$.

The product of the reaction with OH^- ions remains a cobalt(II) derivative, as shown by the rapid uptake of dioxygen after exposing the product solution to air [the amount of O_2 consumed is roughly equal to that required by a Co(II) → Co(III) oxidation]. The characteristic ESR signal of the original $Co(Hdmg)_2$ disappears at about the same rate as the reaction with OH^- occurs. No new ESR signal can be detected either at room temperature or at 77 K, which indicates a possible high-spin configuration for the product of covalent hydration.

A similar type of reaction was recently observed by Brown [11] for methylaquacobaloxime (III) in the presence of strong base.

Addition of equivalent $HClO_4$ at the end of the reaction reproduces the original spectra making probable that the reaction is a reversible "covalent hydration".

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