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Evidence for a S_NCB Mechanism in the Axial Water Substitution Reactions of some Organocobaloximes

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The kinetics of axial ligation by ammonia of some organometallic complexes $RCo(DH)_2H_2O$ ($R = CH_3$, CH_2Cl, C_2H_5) were studied in aqueous solution as a function of the hydroxide ion concentration. The kinetic data indicate that a conjugate base mechanism is operative. The behaviour of these complexes in basic medium is interpreted as the result of two counterbalancing effects: a decrease in reactivity due to the formation of the inert hydroxocomplex, and an enhancement in the reactivity due to the formation of the conjugate base, identified as the species deprotonated at the equatorial ligand system.

Introduction

Previous work has shown that a conjugate base mechanism involving deprotonation of the equatorial system satisfactorily accounts for the pH-dependent water substitution reactions of $RCo[(DO)(DOH)pn]\cdot H_2O^+$ complexes (Fig. 1) [1]. Furthermore it has been suggested that the same reaction scheme could be extended to other aquocomplexes with planar chelating rings containing a potentially acidic function. The $RCo(DH)_2H_2O$ complexes, organocobaloximes, (Fig. 1) behave as weak monoprotic acids in aqueous solution but evidence has been given at

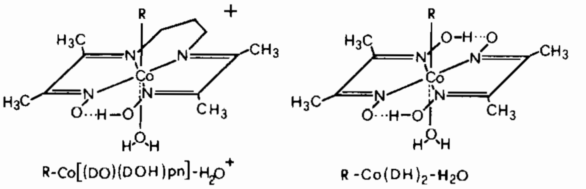
$$RCo(DH)_2H_2O \xrightleftharpoons{K_a} RCo(DH)_2OH^- + H^+ \qquad (1)$$

higher pH values for an additional proton dissociation, from the hydrogen bond of the equatorial chelating ring when $R = CH_2CN$ or CF_3CH_2 [2]. The basic hydrolysis reactions of these complexes occur via a S_NCB mechanism

$$RCo(DH)_2L + OH^- \rightleftarrows RCo(D_2H)L^- + H_2O \qquad (2)$$

$$RCo(D_2H)L^- + H_2O \rightarrow RCo(DH)_2OH^- + L \qquad (3)$$

the rate constant of the aquation of the conjugate base being about 3 times greater than that of the parent compound [2].



$R\text{-}Co[(DO)(DOH)pn]\text{-}H_2O^+$ $\qquad$ $R\text{-}Co(DH)_2\text{-}H_2O$

Fig. 1.

In the present work we examine the axial water substitution reactions of some organocobaloximes in alkaline solution and show that a conjugate base mechanism is consistent with all the kinetic results.

Experimental

The organocobaloximes were prepared as previously reported [3]. Ammonia solutions were standardized by potentiometric titration against HCl. The reactions were monitored by following changes in absorbance in the range 450–500 nm. The pseudo first order rate constants were obtained from the linear plots of $\log(A - A_\infty)$ *vs.* time. Generally 5×10^{-4} *M* solutions of complex were used. The kinetic runs were performed with the use of a Durrum-Gibson stopped flow spectrophotometer.

The spectrophotometric titration was performed with a Perkin Elmer 356 double beam–double wavelength spectrophotometer.

For pH measurements a Radiometer pH-meter Type pH M4 was used.

Results

The effect of the hydroxide ions on the rate of substitution of the axial water by ammonia for the complexes $RCo(DH)_2H_2O$, with $R = CH_3$, C_2H_5, CH_2Cl, is studied.

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TABLE I. Summary of Kinetic Data for the Reaction $RCo(DH)_2H_2O + NH_3$ at Various pH Values.

R	k_1 (M^{-1} s^{-1})	K (M^{-1})	k_2 (s^{-1})	$[OH^-]$ (M)	$[NH_3]$ range (M)
CH_2Cl	1.76 ± 0.04	0.23 ± 0.04		10^{-5}	1.0×10^{-2}–1.0
	1.14 ± 0.02	0.17 ± 0.02		5.0×10^{-3}	1.0×10^{-2}–1.0
	0.96 ± 0.04	0.12 ± 0.01		1.0×10^{-2}	8.8×10^{-3}–8.8×10^{-1}
	0.66 ± 0.02	0.08 ± 0.06		5.0×10^{-2}	1.0×10^{-1}–1.0
	0.57 ± 0.01	0.03 ± 0.02		1.0×10^{-1}	1.0×10^{-1}–1.0
	0.58 ± 0.02	0.05 ± 0.05		2.0×10^{-1}	2.0×10^{-1}–1.0
CH_3	(1.18 ± 0.01) × 10	0.22 ± 0.02		10^{-5}	5.9×10^{-2}–1.1
	(1.13 ± 0.02) × 10	0.12 ± 0.03		5.0×10^{-3}	1.0×10^{-2}–1.0
	(1.04 ± 0.02) × 10	0.12 ± 0.04		1.0×10^{-2}	8.8×10^{-3}–8.8×10^{-1}
	(0.87 ± 0.02) × 10	0.08 ± 0.04		5.0×10^{-2}	1.0×10^{-2}–1.0
	(0.67 ± 0.01) × 10	0.05 ± 0.02		2.0×10^{-1}	2.0×10^{-2}–1.0
	(0.66 ± 0.01) × 10	0.09 ± 0.04		5.0×10^{-1}	8.0×10^{-2}–8.2×10^{-1}
C_2H_5	(2.05 ± 0.03) × 10^2	0.22 ± 0.04		10^{-5}	1.0×10^{-2}–5.0×10^{-1}
	(1.76 ± 0.01) × 10^2		(1.0 ± 0.3) × 10^{-1}	5.0×10^{-2}	1.0×10^{-2}–5.0×10^{-2}
	(1.66 ± 0.01) × 10^2		(1.9 ± 0.4) × 10^{-1}	8.0×10^{-2}	1.0×10^{-2}–5.0×10^{-2}
	(1.62 ± 0.02) × 10^2		(2.1 ± 0.8) × 10^{-1}	1.25×10^{-1}	1.0×10^{-2}–5.0×10^{-2}
	(1.50 ± 0.02) × 10^2		(3.6 ± 0.5) × 10^{-1}	2.0×10^{-1}	1.0×10^{-2}–5.0×10^{-2}
	(1.47 ± 0.02) × 10^2		(6.1 ± 0.7) × 10^{-1}	5.0×10^{-1}	1.0×10^{-2}–5.0×10^{-2}

Data collected at T = (25 ± 0.2) °C, I = 1 M ($NaNO_3$).

$$RCo(DH)_2H_2O + NH_3 \rightleftarrows RCo(DH)_2NH_3 + H_2O \quad (4)$$

These complexes behave as weak acids in aqueous solution (eqn. 1), with $pK_a = 11.95$ for $R = CH_2Cl$, 12.68 for $R = CH_3$, 12.97 for $R = C_2H_5$ [2].

The water substitution reactions of some organocobaloximes by ammonia at pH 9.0 have been previously studied [4]. At this pH value the complexes are almost completely in solution as aquocomplexes.

It has been shown that these reactions involve a prior association between substrate and ammonia. The dependence of the observed pseudo first order rate constant, k_{obs}, upon the concentration of NH_3 is given by the rate law of eqn. 5

$$k_{obs} = \frac{k_1[NH_3]}{1 + K[NH_3]} \quad (5)$$

The kinetic runs were performed in the presence of a high excess of incoming ligand. Under these conditions no significant intercept was found, indicating complete conversion of reactants to products.

In this work the pH of the solutions was varied by addition of appropriate amounts of standard NaOH in the range $[OH^-] = 5 \times 10^{-3}$–$0.5$ M. The range was limited to 0.2 M for the chloromethyl derivative owing to the relatively rapid alkaline decomposition of this complex [2]. At these pH values a significant amount of hydroxocomplex is present in solution.

For the methyl and chloromethyl derivative the dependence of k_{obs} on $[NH_3]$ is given by eqn. 5 at all the pH values studied. Plots of $[NH_3]/k_{obs}$ *vs.* $[NH_3]$ are linear and allow the calculation of k_1 and K. The values of k_1 and K together with the experimental conditions are summarized in Table I. The rate law of eqn. 5 is also observed by the ethyl derivative in the experiment performed at pH 9.0. At higher pH values, when the reactions were performed at lower concentrations of NH_3, a linear dependence of k_{obs} on $[NH_3]$ is observed:

$$k_{obs} = k_2 + k_3[NH_3] \quad (6)$$

Therefore it can be seen that both eqn. 5 and eqn. 6 are special cases of eqn. 7:

$$k_{obs} = \frac{k_1[NH_3]}{1 + K[NH_3]} + k_2 \quad (7)$$

Equation 5 is observed when $[NH_3]$ is sufficiently high to prevent the back reaction, *i.e.* to make $k_1[NH_3]/(1 + K[NH_3]) \gg k_2$; eqn. 6 is observed when $[NH_3]$ is insufficient to make $K[NH_3]$ significant with respect to 1. Hence $k_1 = k_3$ and the k_2 values refer to the hydrolysis reaction. The k_1 and k_2 values are listed in Table I.

TABLE II. Summary of Kinetic Data for the NH_3 Ligation Reactions.[a]

R	$k_A = a\ (M^{-1}\ s^{-1})$	$k_BK_2 = b\ (M^{-2}\ s^{-1})$	$K_1 + K_2 = c\ (M^{-1})$	Q	$[OH^-]$ range (*M*)	$K_1{}^c\ (M^{-1})$
CH_2Cl	1.76 ± 0.04[b]	$(1.1 \pm 0.1)\ 10^2$	$(2.1 \pm 0.1)\ 10^2$	0.30	5×10^{-3}–0.8	112.2[d]
CH_3	$(1.18 \pm 0.01)\ 10$[b]	$(2.3 \pm 0.4)\ 10^2$	$(3.5 \pm 0.3)\ 10$	0.55	5×10^{-3}–0.5	20.9[d]
C_2H_5	$(2.05 \pm 0.03)\ 10^2$[b]	$(2.1 \pm 0.2)\ 10^3$	$(1.5 \pm 0.1)\ 10$	0.68	5×10^{-2}–0.5	13.5[d]

[a] Data at 25 ± 0.1 °C, I = 1 *M* ($NaNO_3$). [b] Measured at pH 9.3 [c] The K_1 values refer to the reaction $RCo(DH)_2H_2O + OH^- \rightleftarrows RCo(DH)_2OH^- + H_2O$ and are related to K_a by expression $K_1 = K_a/K_w$. [d] From the pK_a values of ref. 2.

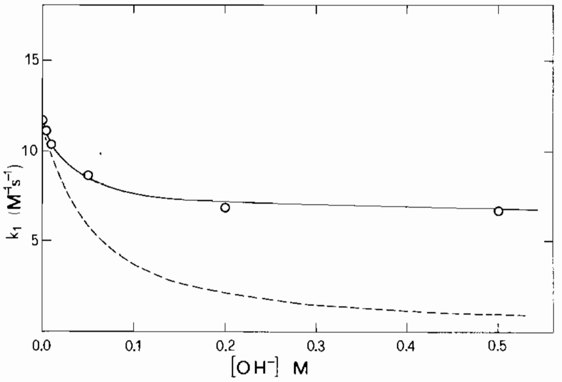


Fig. 2. Plot of k_1 *vs.* $[OH^-]$ for the reaction $CH_3Co(DH)_2$-$H_2O + NH_3$. The solid curve is calculated from eqn. 12 using the parameters of Table II. The dashed curve is calculated from eqn. 15.

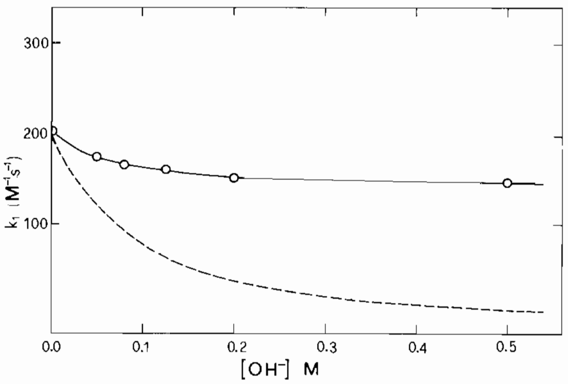


Fig. 4. Plot of k_1 *vs.* $[OH^-]$ for the reaction $C_2H_5Co(DH)_2$-$H_2O + NH_3$. The solid curve is calculated from eqn. 12 using the parameters of Table II. The dashed curve is calculated from eqn. 15.

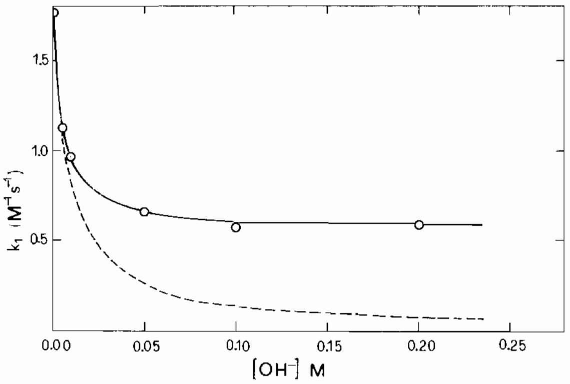


Fig. 3. Plot of k_1 *vs.* $[OH^-]$ for the reaction CH_2ClCo-$(DH)_2H_2O + NH_3$. The solid curve is calculated from eqn. 12 using the parameters of Table II. The dashed curve is calculated from eqn. 15.

For all three complexes examined the k_1 values are dependent on $[OH^-]$ in a non-linear way (Figs. 2–4). Good values for the intercept $k_1 = a$ were obtained by carrying out the reactions in buffered medium (NH_3, NH_4NO_3) at pH about 9.0, where the reaction rate becomes independent of hydroxide ion concentration. The kinetic data are consistent with the expression for k_1 for all these complexes

$$k_1 = \frac{a + b[OH^-]}{1 + c[OH^-]} \tag{8}$$

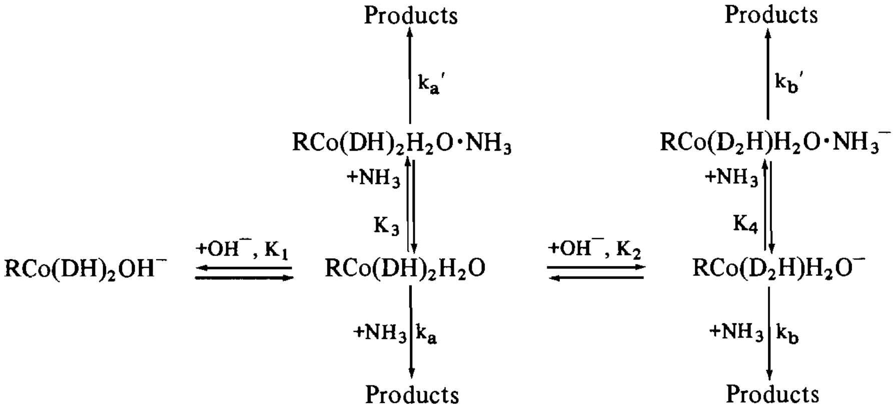
The values of b and c were calculated from the linear plots of $1/(k_1 - a)$ *vs.* $1/[OH^-]$ (Table II).

The K values (eqn. 5) for the methyl and chloromethyl derivative decrease in alkaline solution, but owing to the relatively high uncertainties in the data, we have not attempted to fit an algebraic expression.

The k_2 values (eqn. 6), which are generally too small to be accurately determined increase in a non-linear way with $[OH^-]$.

Discussion

The results of the present work indicate that a conjugate base mechanism can satisfactorily account for the pH-dependent water substitution reactions of the organocobaloximes by ammonia (Scheme I).



Scheme 1

The corresponding kinetic expression is

$$k_{obs} = \frac{\{k_A + k_B K_2[OH^-]\}[NH_3]}{1 + (K_1 + K_2)[OH^-] + K_3[NH_3] + K_2K_4[OH^-][NH_3]} \tag{9}$$

with

$$k_A = k_a + k_a'K_3 \tag{10}$$

$$k_B = k_b + k_b'K_4 \tag{11}$$

If, as suggested, the non-associated form is the reactive one [4], k_A reduces to k_a and k_B to k_b, but the algebraic form of k_{obs} (eqn. 9) is unaltered. Expression 9, at $[OH^-]$ = constant, agrees completely with eqn. 5, with

$$k_1 = \frac{k_A + k_B K_2[OH^-]}{1 + (K_1 + K_2)[OH^-]} \tag{12}$$

$$K = \frac{K_3 + K_2K_4[OH^-]}{1 + (K_1 + K_2)[OH^-]} \tag{13}$$

Furthermore the k_1 dependence on $[OH^-]$, as described by expression 12, is in complete agreement with the empirical expression 8, with $a = k_A$, $b = k_B$-K_2 and $c = K_1 + K_2$.

We have previously suggested that the reactivity in alkaline solution of the cobalt chelates which undergo water substitution via a S_NCB mechanism is the result of two counter-balancing effects [1]. A decrease in the rate is to be expected owing to the formation of the hydroxocomplex, which is generally inert towards the substitution reactions [5–7], while an increase in reactivity should be the consequence of the formation of the conjugate base. The resulting effect may consist either in an increase or in a decrease of the reactivity in basic medium, *i.e.*

$$k_1 = \frac{k_A + k_B K_2[OH^-]}{1 + (K_1 + K_2)[OH^-]} \gtrless k_A \tag{14}$$

and may be better expressed by means of the ratio $Q = k_B K_2/k_A$ $(K_1 + K_2)$. If Q is greater than 1, an acceleration in the rate is observed in alkaline medium (*cf.* C_2H_5 and C_6H_5Co $[(DO)(DOH)pn]$-H_2O^+ [1]); if Q is equal to 1, the rate is independent of $[OH^-]$ (*cf.* $CH_3Co[(DO)(DOH)pn]H_2O^+$ [1]); if Q is less than 1 a rate retardation is observed in basic solution. For the examined organocobaloximes Q is less than I (Table II), so that these complexes show a decrease in reactivity in basic medium. However this decrease would be much greater if the conjugate base were not present (Figs. 2–4). In this hypothesis

$$k_1 = k_A/(1 + K_1[OH^-]) \tag{15}$$

and Q = 0. The relatively low reactivity in basic medium of the organocobaloximes may be due both to the scarce formation of the conjugate base (*i.e.* a low K_2 value) and to the low reactivity of the conjugate base itself (*i.e.* a low k_B value).

No attempt has been made to obtain the K_2 values by subtracting the K_1 values deduced from spectrophotometric measurements [2] from K_1 + K_2. In fact it is commonly accepted that the determination of the equilibrium constants by kinetic methods has an inherently low accuracy, which may be considerably worse than suggested by the standard error owing to systematic errors. On the other hand the spectrophotometric titration of $CH_3Co(DH)_2H_2O$ complexes with NaOH shows good isosbestic points in both visible and U.V. regions up to pH 13.5, indicating that only the deprotonation of the axial water occurs in this pH range. At higher pH values the alkaline decomposition becomes rather fast, as previously observed [2]. This precludes a further examination. Consequently we are only able to place an upper limit on the K_2 values, which should be at least one order of magnitude less than K_1. This lack of a reliable value for K_2 precludes the calculation of k_B (as b/K_2). However the hypothesis of a relatively low reactivity of the deprotonated species is in accord with the fact that in the base hydrolysis the ratio of the aquation rate constants of the conjugate base to those of the parent compound is rather small for these complexes (about 2–3, whereas it is about 100 for the structurally related $RCo[(DO)(DOH)pn]H_2O^+$ complexes [1, 2]).

As far as the K values are concerned, eqn. 12 indicates that they decrease in alkaline solution (as it really occurs) provided that the ratio $K_2K_4/K_3(K_1 + K_2)$ is less than 1.

Scheme 1 is the most simple scheme which is consistent with all the kinetic results. In fact the alternative hypothesis, that the hydrocomplex itself is reactive towards the substitution reactions:

$$RCo(DH)_2OH^- + NH_3 \rightarrow RCo(DH)_2NH_3 + OH^- \qquad (16)$$

which is also in contrast with the general inertness of the hydroxocomplex [5–7], can be ruled out on the basis of the microscopic reversibility principle [1] as the hydrolysis reaction kinetics of the organocobaloximes are not consistent with a bimolecular process. In fact it is well established that the base hydrolysis reactions of these complexes occur via a conjugate base mechanism [2] and the non-linear dependence of k_2 on $[OH^-]$ for the ethyl derivative ensures that this mechanism is also operative in the present case.

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