Inorganica Chimica Acta, 70 (1983) 83–86

Kinetic Evidences for Pre-equilibria in the Substitution Reactions of Alkylbis(dimethylglyoximato)aquocobalt(III) Complexes in Aqueous Solution

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Received July 10, 1980

Kinetics of the water substitution reactions of some organometallic complexes $RCo(DH)_2H_2O$ ($R = CH_3$, CH_2Cl, CF_3CH_2) were studied in aqueous solution (DH_2 = dimethylglyoxime). Nucleophiles used included NH_3, imidazole, morpholine and SCN^-. The results are consistent with a mechanism involving the direct replacement of coordinated water. Prior association of the alkylaquocobaloxime with some ligands (NH_3, imidazole, morpholine) is evidenced using high nucleophile concentrations. Some hypotheses on the nature and the reactivity of the intermediate are made.

Introduction

The kinetics of substitution of axial water of alkylaquocobaloximes in aqueous solutions have been extensively studied. The strictly second order kinetics (first order in complex and first order in nucleophile) and the narrow range of the rate constants on reactions with various incoming ligands, suggest that the substitution process is an I_d mechanism. Evidence for intermediates of reduced coordination number has not been given, but the data do not preclude the possibility of a D mechanism, in which water behaves as a more efficient nucleophile than the incoming ligand.

For the reaction of ethylaquocobaloxime with hexacyanometalates [1], a mechanism is proposed involving a prior outer sphere association of the cobaloxime with $M(CN)_6^{n-}$, followed by the rate determining loss of water. It is suggested that a possible mode of interaction is a hydrogen bond between the coordinated water molecule and the nitrogen of a cyanide.

A prior association mechanism has been proposed also for the structurally related $RCo[(DO)(DOH)pn]H_2O^+$ complexes in their reactions with ligands containing aromatic groups [2]. It is suggested that the intermediates are formed through a π–π interaction with the conjugated system of the [(DO)(DOH)pn] ligand.

In this work we examine the water substitution reactions of some alkylbis(dimethylglyoximato)aquocobalt(III) complexes at high concentrations of nucleophile, in order to verify if the prior association mechanism is also operative for ligands other than hexacyanometalates.

Experimental

Materials

The organocobaloximes were prepared as previously reported [3]. All other chemicals were analytical grade and used without further purification. Ammonia and morpholine solutions were standardized by potentiometric titration against HCl. Sodium thiocyanate solutions were standardized by titration with $AgNO_3$. The imidazole solutions were prepared from a known weight of reagent.

Instruments

The faster reactions were followed with use of a Durrum stopped flow spectrophotometer. The slower kinetic runs were performed with a Perkin Elmer model 356 double beam–double wavelength spectrophotometer.

For pH measurements a Radiometer pH meter type pHM4 equipped with a glass and calomel electrode was used.

Results

The substitution reactions of the coordinated water in some cobaloximes were studied at high concentration of the incoming ligand:

$$RCo(DH)_2H_2O + L \rightarrow RCo(DH)_2L + H_2O \tag{1}$$

with

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TABLE I. Summary of Kinetic Data for the Reactions $RCo(DH)_2H_2O + NH_3$*.

R	a (M^{-1} s^{-1})	b (M^{-1})
CH_3	16.6 ± 0.5	0.34 ± 0.03
CH_2Cl	2.44 ± 0.07	0.44 ± 0.03
CF_3CH_2	(7.3 ± 0.2) 10^{-2}	0.31 ± 0.03

*Data at 25 ± 0.2 °C, I = 2.5 *M* ($NaNO_3$), pH ≅ 9.0.

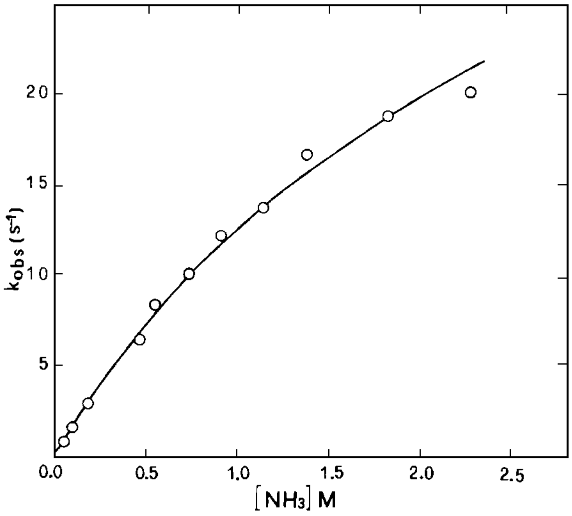

Fig. 1. Plot of k_{obs} *vs.* [NH_3] at pH ≅ 9.0, I = 2.5 *M* ($NaNO_3$), 25 °C for the reaction $CH_2ClCo(DH)_2H_2O + NH_3$. The solid curve is calculated from eqn. 2 using the calculated parameters of Table I.

R = CH_3, CH_2Cl, CF_3CH_2
L = NH_3, imidazole, morpholine, SCN^-

The kinetic measurements were performed in aqueous solution at I = 2.5 *M* ($NaNO_3$). The initial concentration of the complexes was 0.5–1.0 X 10^{-3} *M*. The ligand concentrations range from 1 X 10^{-2} to 2.5 *M* for NH_3, 1.25 *M* for SCN^-, 1.0 *M* for morpholine and imidazole.

The pK_a of the coordinated water is 12.68 for $CH_3Co(DH)_2H_2O$, 11.95 for $CH_2ClCo(DH)_2H_2O$ and 10.96 for $CF_3CH_2Co(DH)_2H_2O$ [4]. Consequently when the incoming ligand was NH_3 (pK_a = 9.43, [5]) or morpholine (pK_a = 8.70, [6]) it was necessary to buffer the solution. This was obtained by addition of a half equivalent of HNO_3 to a solution of free base. The resulting pH was about 9.0. At this pH value the complexes are almost completely in the form of aquocomplexes. Furthermore at the concentrations used the ligand dissociation is negligible.

TABLE II. Summary of Kinetic Data for the Reactions $CH_2ClCo(DH)_2H_2O + L$.*

L	a (M^{-1} s^{-1})	b (M^{-1})
Morpholine**	2.1 ± 0.1	0.58 ± 0.09
Imidazole	20.9 ± 0.9	1.08 ± 0.09
SCN^-	37.8 ± 0.8	

*Data at 25 ± 0.2 °C, I = 2.5 *M* ($NaNO_3$). **Ligand solutions buffered at pH ≅ 9.0.

TABLE III. Kinetic Data for the Reactions $CH_2Cl\ Co(DH)_2H_2O + NH_3$ at Various Temperatures.*

t °C	a (M^{-1} s^{-1})	b (M^{-1})
16.1	0.64 ± 0.01	0.31 ± 0.05
22.2	1.24 ± 0.04	0.25 ± 0.08
25.0	1.76 ± 0.04	0.23 ± 0.04
24.0	2.67 ± 0.01	0.53 ± 0.01
35.3	5.02 ± 0.07	0.33 ± 0.06
42.4	9.7 ± 0.2	0.32 ± 0.06

*Data at I = 1 *M* ($NaNO_3$), pH ≅ 9.0, [NH_3] range = 0.1–0.5 *M*.

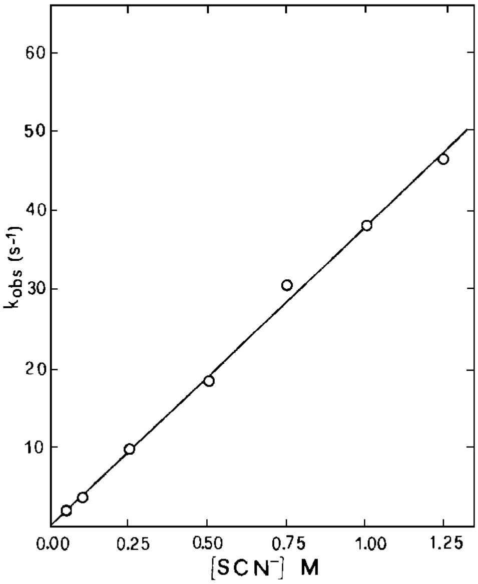

Fig. 2. Plot of k_{obs} *vs.* [SCN^-] at I = 2.5 *M* ($NaNO_3$), 25 °C for the reaction $CH_2ClCo(DH)_2H_2O + SCN^-$.

The observed pseudo first order rate constants, k_{obs}, were obtained from the linear plots of log (A – A_∞) *vs.* time.

When L = NH_3, morpholine, imidazole, the values of k_{obs} are dependent on [L] in a nonlinear way (Fig. 1) according to the expression:

$$k_{obs} = a[L]/(1 + b[L]) \tag{2}$$

Plots of $[L]/k_{obs}$ *vs.* [L] were found to be linear and allow the calculation of a and b (Tables I, II).

When L = SCN^- a linear plot of k_{obs} *vs.* [L] is obtained (Fig. 2):

$$k_{obs} = c[L] \tag{3}$$

It is reasonable to assume that eqn. 3 is a special case of eqn. 2 for $b[L] \ll 1$, so that c = a (Table II).

Furthermore the reaction between $CH_2ClCo(DH)_2H_2O$ and NH_3 was studied at various temperatures in the range 16–42.4 °C. The temperature was maintained constant within ±0.2 °C. At all temperatures the dependence of k_{obs} on $[NH_3]$ is adequately described by eqn. 2. Values of a and b are summarized in Table III, together with the experimental conditions.

Discussion

The general rate law of eqn. 2 is consistent both with a D mechanism and with a reaction mechanism involving a pre-equilibrium preceding the rate determining step.

For the former mechanism

$$RCo(DH)_2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCo(DH)_2 + H_2O \tag{4}$$

$$RCo(DH)_2 + L \xrightarrow{k_2} RCo(DH)_2L \tag{5}$$

the expression of k_{obs}, assuming a steady state for $RCo(DH)_2$, becomes:

$$k_{obs} = \frac{(k_1k_2/k_{-1})\,[L]}{1 + (k_2/k_{-1})\,[L]} \tag{6}$$

This agrees completely with eqn. 2, with $a = k_1k_2/k_{-1}$ and $b = k_2/k_{-1}$.

For the latter mechanism

$$RCo(DH)_2H_2O + L \overset{K}{\rightleftharpoons} RCo(DH)_2H_2O\cdot L \tag{7}$$

$$RCo(DH)_2H_2O + L \xrightarrow{k_3} RCo(DH)_2L + H_2O \tag{8}$$

$$RCo(DH)_2H_2O\cdot L \xrightarrow{k_4} RCo(DH)_2L + H_2O \tag{9}$$

the expression

$$k_{obs} = \frac{(k_3 + k_4K)\,[L]}{1 + K\,[L]} \tag{10}$$

is also in agreement with eqn. 2, with $a = k_3 + k_4K$ and $b = K$.

The first scheme must be rejected, as the k_1 values (= a/b) are strongly dependent on the nature of L, contrary to the expectation for a purely dissociative mechanism [7]. Thus the prior association mechanism should be operative. Prior associations in aqueous solution have been observed in the reactions of ethylaquocobaloxime with hexacyanometalates [1] and in the reactions of the structurally related $RCo[(DO)(DOH)pn]H_2O^+$ with aromatic ligands [2]. It appears that the phenomenon can be observed also in presence of other ligands, when their concentration is sufficiently high. Although the cause of the interaction between substrate and Lewis base cannot be unambiguously established, some considerations can be made. The extent of the prior association, as expressed by the K (=b) values (Tables I, II), is dependent on the nature of the incoming ligand and decreases in the order imidazole > morpholine $\geqslant$ NH_3. No prior association is observed for SCN^- in the range of concentrations examined. This suggests that the interaction between the substrate and the nucleophile cannot be caused by electrostatic or polarization forces, because the charged ligand does not interact with the uncharged complex. Furthermore the K values are practically independent of temperature (Table III). On the contrary, in the reactions of the ethylaquocobaloxime with hexacyanometalates [1], the value of the prior association constant for the more negatively charged $Fe(CN)_6^{4-}$ ion is considerably larger than that for the $M(CN)_6^{3-}$ ions (M = Fe(III), Co(III), Cr(III)) and is strongly dependent on temperature.

On the other hand, not all the incoming ligands contain aromatic groups, so that the interaction must differ from that occurring in the water substitution reactions of $RCo[(DO)(DOH)pn]H_2O^+$ complexes, attributed to a π–π interaction between the aromatic ligand and the chelating ring [2].

A possible mode of interaction is a hydrogen bond between chelate and nucleophile. As the K values are insensitive to the nature of the R group (Table I), it is probable that the association occurs at the planar chelating ring, *i.e.* in *cis* position to the R group. In fact a strong effect of the nature of R would be expected [4] if the *trans* position were involved. It has been suggested that in methyl(piperidine)cobaloxime the hydrogen bond of the chelating ring is disrupted by addition of a Lewis base and that a new hydrogen bond between the dimethylglyoximate ligand and the Lewis base is formed [8]. The hypothesis that a similar interaction occurs also in the present case is in accord with the observation that the extent of the prior association decreases in strongly alkaline medium [9]. We suggest that under the latter conditions the deprotonation of the equatorial ligand occurs, which prevents the formation of intermolecular hydrogen bonds.

On the basis of the expression of k_{obs} it is not possible to decide whether both $RCo(DH)_2H_2O$ and $RCo(DH)_2H_2O \cdot L$ or only one of the two species make an appreciable contribution to the observed rate. However, if the prior association occurs at the planar chelating ring, the distance of the interaction site from the coordination position leads us to think that the associated form could be an unreactive species and that path 8 could be the main reaction pathway. This suggestion is further supported by the observation that chloromethylcobaloxime is quite reactive towards axial substitution also in the reaction with SCN^-, where the pre-equilibrium is not evident *i.e.* K is very small or zero (Table II).

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