Mechanistic Informations from *trans*-Effect in the Anation Reactions of some Bis(dimethylglyoximato)Rh(III) Complexes

R. DREOS GARLATTI*, G. TAUZHER and G. COSTA

Dipartimento di Scienze Chimiche, Università di Trieste, P. le Europa 1, 34127 Trieste, Italy

Received March 12, 1986; revised June 2, 1986

Abstract

The parallel lability trend for the anation reactions of $RRh(DH)_2H_2O$ ($R = CH_3$, CH_3CH_2, CF_3CH_2, $ClCH_2$) and $RCo(DH)_2H_2O$ complexes suggests a dissociative activation process for the reactions of the organorhodoximes. The high lability of these complexes, arising from the stabilization of the transition state, is not entirely due to the *trans*-effect of the R group, but, at least partially, to the labilizing effect of the equatorial macrocycle.

Introduction

In our previous work we examined the anation reactions of $CH_3Rh(DH)_2H_2O$ by various incoming ligands [1].

$$CH_3Rh(DH)_2H_2O + L \rightleftharpoons CH_3Rh(DH)_2L + H_2O \quad (1)$$

Two unexpected features were evidenced:

(i) The reactions of $CH_3Rh(DH)_2H_2O$ are very fast, about 60 times faster than the corresponding reactions of $CH_3Co(DH)_2H_2O$.

(ii) The anation rate constants are almost independent of the nature of the incoming ligands, suggesting a dissociative activation process, but the ΔS^* value, which was determined for the reaction with thiourea, is largely negative, suggesting a certain degree of participation of the incoming ligand to the transition state.

In order to obtain further insight into the causes of the lability and the activation mode for these complexes, we examine in the present work the substitution reactions of some rhodoximes** containing different non-labile axial groups.

Experimental

Preparation of Complexes

(i) The organometallic derivatives were prepared by an adaptation of the previously reported synthesis of $CH_3Rh(DH)_2H_2O$ [2, 3].

0.2 g of dichlorocomplex, prepared by standard methods [4], was suspended in 20 ml of aqueous methanol (70% methanol). A NaOH solution (5 mmol in 5 ml of H_2O) was added to dissolve the starting material and nitrogen was bubbled through the stirred solution. After 10 min the complex was reduced by adding a stoichiometric amount of $NaBH_4$ dissolved in water. The solution became black but turned yellow after the addition of about threefold molar excess of alkylating agent (RI or RBr). After 30 min the solution was filtered to remove eventual solid residuals, diluted to 50 ml with methanol and neutralized with $HClO_4$ 1 M. By evaporation of methanol a brown-orange precipitate was obtained whose analytical composition corresponds to $RRh(DH_2)(DH)X$ (Table I).

Conductometric titration with $AgNO_3$ confirms the presence of one equivalent of halogenide for one mole of complex.

In order to obtain the aquoderivatives, the halogenocomplexes were dissolved in the least amount of methanol and a stoichiometric amount of $AgClO_4$ dissolved in water was added. The resulting suspension was stirred for about five minutes and then filtered off. The volume of the clear filtrate was reduced in a rotary evaporator until precipitation began. Yellow crystals of $RRh(DH_2)(DH)H_2O^+ClO_4^-$ were obtained by allowing the solution to stand (Table I).

(ii) $(C_6H_5)_3PRh(DH)_2Cl$ was obtained by the procedure described by Powell [5].

Reagents

All other materials were analytical grade and used without further purification.

*Author to whom correspondence should be addressed.

**Rhodoximes is the name given to bis(dimethylglyoximato)Rh(III) complexes by analogy to cobaloximes [2].

0020-1693/86/$3.50

TABLE I. Analytical Data

	C (%)		H (%)		N (%)	
	calc	found	calc	found	calc	found
$CH_3Rh(DH_2)(DH)I$	22.7	22.6	3.8	3.6	11.4	11.7
$CH_3CH_2Rh(DH_2)(DH)I$	24.5	24.4	4.1	4.1	11.8	11.5
$ClCH_2Rh(DH_2)(DH)Br$	23.3	23.4	3.6	3.5	12.1	12.0
$CF_3CH_2Rh(DH_2)(DH)I$	21.3	22.0	3.4	3.1	9.8	10.3
$CH_3Rh(DH_2)(DH)H_2O^+NO_3^-$	25.2	25.4	4.7	4.7	16.3	15.9
$CH_3Rh(DH_2)(DH)H_2O^+ClO_4^-$	23.2	23.3	4.3	4.6	12.0	11.9
$CH_3CH_2Rh(DH_2)(DH)H_2O^+ClO_4^-$	25.0	25.3	4.6	4.8	11.6	10.9
$ClCH_2Rh(DH_2)(DH)H_2O^+ClO_4^-$	21.5	22.1	3.8	4.3	11.2	10.6
$CF_3CH_2Rh(DH_2)(DH)H_2O^+ClO_4^-$	22.4	22.1	3.6	3.3	10.5	9.2
$CH_3CH_2CH_2Rh(DH_2)(DH)H_2O^+ClO_4^-$	26.7	26.9	4.9	4.9	11.3	11.8

Instruments

For pH measurements a radiometer pH M4 was used. The equilibrium studies and the kinetics of the hydrolysis reactions were performed with a Perkin Elmer 356 spectrophotometer. The water substitution kinetics were followed with use of a Hi-Tech SF 3 series stopped flow spectrophotometer.

Data Analysis

The computer program used for the least squares analysis was Statistical Package for Social Sciences, version 9 (Vogelback Computing Center, Northwestern University, U.S.A.).

Results

(1) Equilibrium Studies

(i) As outlined in Experimental, the organometallic complexes were isolated in the protonated form $RRh(DH_2)(DH)H_2O^+ClO_4^-$.

Potentiometric titrations with NaOH show that these complexes behave as relatively strong acids in aqueous solution.

A K_1 value of 0.18 ± 0.08 M for the equilibrium

$$CH_3Rh(DH_2)(DH)H_2O^+ \rightleftharpoons CH_3Rh(DH)_2H_2O + H^+ \quad (2)$$

was previously obtained [2].

(ii) The deprotonation of the axial water of complexes $RRh(DH)_2H_2O$ ($R = CH_3CH_2$, $ClCH_2$, CF_3CH_2) was studied at 20 ± 0.1 °C, in aqueous solution at $I = 1$ M ($NaNO_3$), by means of spectrophotometric titration in the range 370–430 nm. The pK_2 values were calculated by using relation

$$\log[(A - A_0)/(A_\infty - A)] = pH - pK_2 \quad (3)$$

where A is the measured absorbance of the solution in presence of OH^-, A_0 is the absorbance of the aquocomplex and A_∞ is the absorbance of the hydroxocomplex.

The pK_2 values are reported in Table II.

TABLE II. pK_2 values for Equilibrium $RM(DH)_2H_2O \rightleftharpoons RM(DH)_2OH^- + H^+$

at I = 1 M ($NaNO_3$), 20 °C

R	M = Rh(III)	M = Co(III)[b]
CH_3CH_2	9.85 ± 0.01	12.97 ± 0.02
CH_3	9.78 + 0.04[a]	12.68 ± 0.02
CH_2Cl	9.06 ± 0.01	11.95 ± 0.02
CF_3CH_2	8.85 ± 0.01	10.96 ± 0.01

[a]From ref. 1. [b]From ref. 23.

(2) Kinetics

(i) Anation reactions

The anation reactions

$$RRh(DH)_2H_2 + SC(NH_2)_2 \rightleftharpoons RRh(DH)_2SC(NH_2)_2 + H_2O \quad (4)$$

$R = CH_3CH_2$, $ClCH_2$, CF_3CH_2

were studied at various temperatures in the range 4–50 °C. The temperature was maintained constant within 0.1 °C.

The kinetic measurements were performed in aqueous solution at $I = 1$ M ($NaNO_3$) under pseudo first order conditions. The initial concentration of the complexes was $2–4 \times 10^{-4}$ M; the ligand concentrations range from 2×10^{-3} to 2.5×10^{-2} M. Both the complex and the ligand solutions were buffered at pH about 7 (phosphate buffer); at this pH value the complexes are almost completely in the form of aquocomplexes.

The reactions were monitored by following changes in absorbance in the range 370–430 nm.

The observed pseudo first order rate constants (k_{obs}) were obtained from the linear plots of $\log(A_t - A_\infty)$ *versus* time, where A_t is the optical absorbance at time t and A_∞ is the final absorbance.

The k_{obs} values show a linear dependence on thiourea concentration in the range of examined

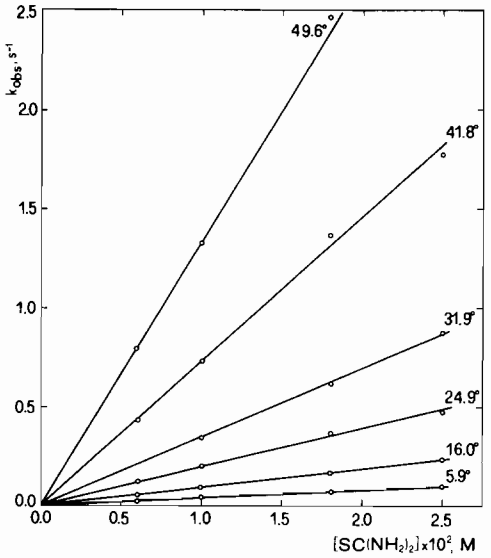

Fig. 1. Dependence of k_{obs} on [thiourea] at various temperatures for the reaction $CF_3CH_2Rh(DH)_2H_2O$ + thiourea.

concentrations (Fig. 1), according to the expression

$$k_{obs} = k_1[SC(NH_2)_2] + k_{-1} \quad (5)$$

Values of k_1 and k_{-1} calculated by a linear least squares analysis are reported in Table III as a function of temperature. Errors are standard deviations; errors on k_1 are of about 2–3% and do not exceed 5–6% for the faster reactions.

TABLE III. Rate Constants for the Anation Reactions at I = 1 M ($NaNO_3$), at Various Temperatures

R	t (°C)	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})
CH_3CH_2	4.9	(1.64 ± 0.08) × 10^4	3.9 ± 4.4
	7.9	(1.82 ± 0.07) × 10^4	10.4 ± 3.8
	10.8	(2.17 ± 0.12) × 10^4	12.5 ± 6.2
	14.0	(2.41 ± 0.07) × 10^4	19.2 ± 3.7
	17.0	(3.08 ± 0.14) × 10^4	33.8 ± 7.4
	20.0	(3.61 ± 0.21) × 10^4	38.5 ± 11.4
CF_3CH_2	5.9	(4.2 ± 0.1)	
	16.0	(9.5 ± 0.1)	
	24.9	(19.2 ± 0.6)	
	31.9	(35.3 ± 1.6)	
	41.8	(72.2 ± 2.1)	
	49.6	(133.0 ± 2.5)	
$ClCH_2$	4.0	(1.15 ± 0.03) × 10^2	
	9.9	(1.65 ± 0.12) × 10^2	
	15.0	(2.67 ± 0.05) × 10^2	
	18.0	(2.47 ± 0.06) × 10^2	
	20.0	(3.12 ± 0.15) × 10^2	0.27 ± 0.18
	24.9	(4.94 ± 0.31) × 10^2	0.94 ± 0.50
	29.9	(5.93 ± 0.20) × 10^2	0.31 ± 0.20

TABLE IV. Anation Rate Constants as a Function of pH

R	t (°C)	k_1 (M^{-1} s^{-1})	pH
CH_3CH_2	5.0	1.69 × 10^4	5.1
		1.62 × 10^4	6.5
		1.65 × 10^4 [a]	7.0
		1.60 × 10^4	7.9
CF_3CH_2	16.0	9.4	5.1
		9.1	5.8
		9.8	6.5
		9.3[a]	7.0
		9.4	7.2
		9.4	7.7
$ClCH_2$	15.0	2.63 × 10^2	5.1
		2.65 × 10^2	5.8
		2.66 × 10^2	6.5
		2.55 × 10^2 [a]	7.0
		2.57 × 10^2	7.2
		2.43 × 10^2	7.7

[a]Calculated from ΔH^* and ΔS^* values of Table V.

As the variation in temperature may cause a significant shift in pH, the anation reactions of CH_3CH_2, $ClCH_2$ and CF_3CH_2 derivatives were examined in the pH range 5.0–7.8, where they were shown to be independent of the pH value (Table IV). The same result has been previously obtained for the methyl derivative [6].

The activation parameters ΔH^* and ΔS^* were calculated by fitting the k_1–T data to the Eyring equation in the exponential form

$$k_1 = (kT/h) \exp(-\Delta H^*/RT) \exp(\Delta S^*/R) \quad (6)$$

by a non linear least squares analysis, each value of k_1 being weighted as $1/\sigma_{k_1}^2$ (Fig. 2).

The ΔH^* and ΔS^* values are reported in Table V.

(ii) Hydrolysis of $(C_6H_5)_3PRh(DH)_2Cl$

In order to test the effect on the lability of rhodoximes of a non-organometallic axial group, the reaction

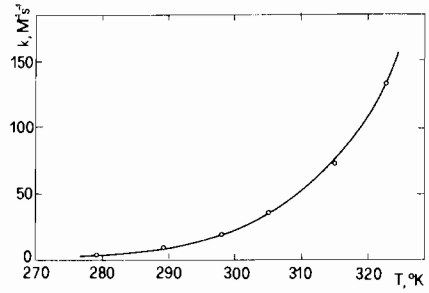

Fig. 2. Dependence of k_1 on T for the reaction $CF_3CH_2Rh(DH)_2H_2O$ + thiourea. The solid line is the computer fit of the data to the Eyring equation.

TABLE V. Activation Parameters for the Reaction $RM(DH)_2H_2O + SC(NH_2)_2 \rightleftharpoons RM(DH)_2SC(NH_2)_2 + H_2O$

R	M = Rh(III)			M = Co(III)[c]		
	log k_1 (20 °C)[a]	ΔH^* (kcal mol^{-1})	ΔS^* (e.u.)	log k_1 (20 °C)[a]	ΔH^* (kcal mol^{-1})	ΔS^* (e.u.)
CH_3CH_2	4.58	8.4 ± 0.3	−8.9 ± 1.0	3.13	14.3 ± 0.7	4.6 ± 2.4
CH_3	3.85[b]	7.7 ± 0.3[b]	−14.6 ± 1.1[b]	1.94	14.6 ± 0.5	0.2 ± 1.1
$ClCH_2$	2.54	10.1 ± 0.4	−12.4 ± 3.8	1.09	16.3 ± 0.3	2.1 ± 1.0
CF_3CH_2	1.12	14.5 ± 0.3	−3.9 ± 1.0	−0.28	18.0 ± 0.1	1.6 ± 0.4

[a]Interpolated from the rate constants determined at temperatures other than 20 °C. [b]From ref. 1. [c]From ref. 14.

$$(C_6H_5)_3PRh(DH)_2Cl + H_2O \longrightarrow (C_6H_5)_3PRh(DH)_2H_2O^+ + Cl^- \quad (7)$$

was studied in mixed solvent methanol (30%)–water(70%) at 25 °C by following changes in absorbance at 300 nm.

The reaction conforms to the first order law

$$-d[complex]/dt = k_{aq}[complex] \quad (8)$$

with $k_{aq} = 2.2 \times 10^{-3}$ s^{-1}.

Discussion

The octahedral Rh(III) complexes are generally inert towards the substitution reactions as, or more than, the corresponding Co(III) complexes [7]. It has been previously shown that the factors which enhance the lability of Co(III) complexes, *i.e.* the presence of an unsaturated chelating ring [8, 9] or of a coordinated alkyl group in *trans* position [10, 11] show an analogous effect in the Rh(III) substitution reactions [1, 12, 13].

A direct comparison is possible in the case of $M(III)(TPPS)(H_2O)_2^{3-}$ (TPPS = *meso*-tetrakis(*p*-sulphonato phenyl)porphine, M = Co, Rh): the reactions of Rh(III) complexes are about four orders of magnitude slower than that of the corresponding Co(III) complexes [12]. For both Rh(III) and Co(III) derivatives the lability of systems containing unsaturated ring has been attributed to the electron donating capability of the equatorial system, making the central metal(III) ion more likely to be a metal(II) ion [8, 9, 12, 13].

As far as the lability of compounds containing coordinated alkyl group is regarded, data of Table V show that the organorhodoximes are more labile than the corresponding Co(III) complexes, the reactivity ratio being about 60 for R = CH_3 and about 20 for R = CH_3CH_2, CF_3CH_2 and $ClCH_2$.

The lability of organocobaloximes, as compared with non-organometallic cobaloximes, is related to low ΔH^* values, the ΔS^* values being about zero [14, 15]. Structural and equilibrium data show that the alkyl groups promote the lengthening of the *trans*-cobalt–water bond with a parallel increase of the pK_2 values [16]. Hence the lability of these complexes is largely due to the weakening of the cobalt–oxygen bond in the ground state.

Data of Table V show that the higher lability of the organorhodoximes relative to the organocobaloximes is caused by lower ΔH^*, the ΔS^* values being strongly negative. Unfortunately no structural data are available for these complexes, but the lower pK_2 values (Table II) suggest a stronger metal oxygen bond in the ground state. (It should be noted that considerable similarity exists between pK_2 values of coordinated water for corresponding Co(III) and Rh(III) systems [6]).

The question immediately follows whether the high lability of these complexes is entirely due to an enhanced kinetic *trans*-effect, which is clearly contrasting with the lower *trans*-influence, or at least partially, to a better transmission of the *cis*-effect of the equatorial ligand. An indication in this sense arises from the comparison of the rate constants for the hydrolysis reactions of the non-organometallic $(C_6H_5)_3PM(III)(DH)_2Cl$ (M = Co, Rh) complexes containing a typical π-acceptor ligand in the *trans*-position. Indeed the reaction of Rh(III) is found about 20 times faster than the reactions of Co(III) in the same experimental conditions ($k_{aq} = 2.2 \times 10^{-3}$ s^{-1} and 1.1×10^{-4} s^{-1} [17], respectively).

Hence also for the bisdimethylglyoximato complexes, as it has been found previously for porphinato derivatives [13], the central metal atom seems to control the extent of labilization induced by the equatorial ligand.

The concurrence of lower ΔH^* and lower pK_2 values for organorhodoximes suggests that the higher lability of Rh(III) complexes is caused by a stabilization of the transition state.

Owing to its ephemeral nature a detailed picture of the transition state is difficult to obtain; this is particularly true in the present case, where the mode of activation itself is not so certain.

Indeed, since the reactions of $RRh(DH)_2H_2O$ complexes show no deviations from second order

kinetics in the range of observed thiourea concentrations (eqn. (5)), there is no kinetic evidence for an intermediate and the stoichiometric mechanism should be classified as I [18].

An interchange mechanism may involve either associative or dissociative activation (I_a or I_d mechanism), according to the relative importance of bond making and bond breaking in the transition state. The evidences which usually lead to the conclusion that a dissociative mechanism is occurring are the independence of the rate constants on the nature of the incoming ligands, the increase of lability with an increase in the electron donor power of the group in the *trans*-position, and the presence of positive ΔS^* values. All these criteria concomitantly indicate that the substitution reactions of Co(III) occur through a dissociative mechanism, but contrasting indications have been obtained for the Rh(III) complexes.

Dissociative activation has been proposed for the anation reactions of $RhCl_n(H_2O)_{6-n}^{3-n}$ [19] and $Rh(en)_2(H_2O)_2^{3+}$ [20], whereas an associative interchange mechanism seems to be operative in the exchange of bound water of $Rh(NH_3)_5H_2O^{3+}$ [21]. The above conclusions have been mainly drawn on the basis of the observed activation entropy. For the anation reactions of $Rh(TPPS)(H_2O)_2^{3-}$ [12] an associative activation process has been tentatively suggested in consideration of the negative ΔS^* values. On the other hand, when the dependence of the reaction rate on the pressure was examined [22] it was concluded that the experimentally observed ΔV^* values were in good agreement with those expected for an interchange mechanism in which the rate determining step is dissociatively activated. Kinetic results indicate that dissociative activation is occurring in the substitution reactions of the strictly related $Rh(TAPP)(H_2O)_2^{5+}$ complex (TAPP = *meso* tetrakis(*p*-trimethylammonium phenyl)porphine) [13].

As pointed out in the introduction a puzzling situation occurs in the substitution reactions of $CH_3Rh(DH)_2H_2O$; the k_1 values vary in a very restricted range by varying the incoming ligands, but the ΔS^* value, which was determined for the reaction with thiourea, is largely negative [1].

In order to obtain further indications on the nature of the activation process, we have examined the effect on the reaction rate of a variation of the R group. Data of Table V show that the lability trend is almost parallel for Co(III) and Rh(III) reactions, strongly suggesting that dissociative activation is operative also for the organoaquorhodoximes.

It is interesting to note that the 2,2,2-trifluoroethyl derivative, which in the Co(III) series is more inert than expected on the basis of the electron donor power of the R group [15, 23], exhibits the same behavior in the Rh(III) series. Structural data relative to organocobaloximes [16, 24] show that the effective bulk of the CF_3CH_2 group is significantly reduced as a consequence of the distortion of the alkyl group itself. The similarity in kinetic behavior suggests that analogous distortions should be present in the CF_3CH_2 group coordinated to the Rh(III) center, in spite of the larger size of this metal ion.

If the substitution reactions of organoaquorhodoximes are occurring through a dissociative activation process, the negative ΔS^* values cannot arise from an interaction with the incoming ligand in the transition state. An alternative hypothesis is that they are determined from an increased solvation in going from the ground to the transition state. Indeed, the hypothesis that the solvent plays an important role in the substitution reactions of these complexes is in accord with our preliminary observation that the substitution rate of methylaquorhodoxime is more affected by the change of the solvent than that of methylaquocobaloxime, the rate constants ratio for the reactions in water and in water(50%)–dioxane(50%) being about 38 for Rh(III) and 2.6 for Co(III) [25].

In order to test the role of the solvent in the Rh(III) substitution reactions more systematic studies in various solvents are planned.

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