Substitution Kinetics of Methylbis(dimethylglyoximato)aquorhodium(III) in Aqueous Solution

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

Istituto di Chimica, Università di Trieste, P.le Europa 1, 34127 Trieste, Italy

Received November 21, 1983

Most of the studies of substitution reactions of octahedral complexes concern Co(III) complexes [1]. The substitution reactions of Rh(III) derivatives have not been studied so extensively, so that a direct comparison of their reactivity with that of the corresponding Co(III) complexes is possible only in few cases. This comparison would be of interest in order to ascertain the effect of increasing size and effective nuclear charge of the central metal atom.

The cobalt(III) complexes are usually inert, but the presence of an unsaturated chelating system [2, 3] or of a σ coordinated alkyl group in a trans position [4, 5] enhances the substitution rate considerably. The causes of labilization in the two cases are very different. The lability of systems containing unsaturated macrocycles has been attributed to the very strong equatorial ligand field, which leads to a loss of d^6 character of the Co(III) center [2, 3]. The lability of organometallic complexes is largely due to the weakening of the bond between the cobalt atom and the ligand *trans* to the alkyl group in the ground state [4–6]. All these reactions occur through a dissociative mechanism [2–5].

Aquation of Rh(III) amines is generally slower than that of Co(III) amines [1]; anation reactions of $Rh(NH_3)_5H_2O^{3+}$ exhibit rate constants of the same order of magnitude as those of $Co(NH_3)_5H_2O^{3+}$ [7]. The labilizing effect of a porphinic ring has been demonstrated in the reactions of (meso-tetrakis(p-sulphonatophenyl)porphinato)diaquorhodate(III), $Rh(TPPS)(H_2O)_2^{3-}$, [8, 9], but these reactions are about four orders of magnitude slower than those of the corresponding Co(III) complex [2]. For the substitution reactions of $Rh(TPPS)(H_2O)_2^{3-}$ [8, 9] and of some other Rh(III) complexes [10] an associative mechanism has been tentatively proposed.

In order to assess the extent of labilization caused by the presence of an alkyl group in trans position in the rhodium derivatives, we have undertaken the study of the reactions of methylbis(dimethylglyoximato)aquorhodium(III) with N_3^-, SCN^-, I^-, pyridine, thiourea (L):

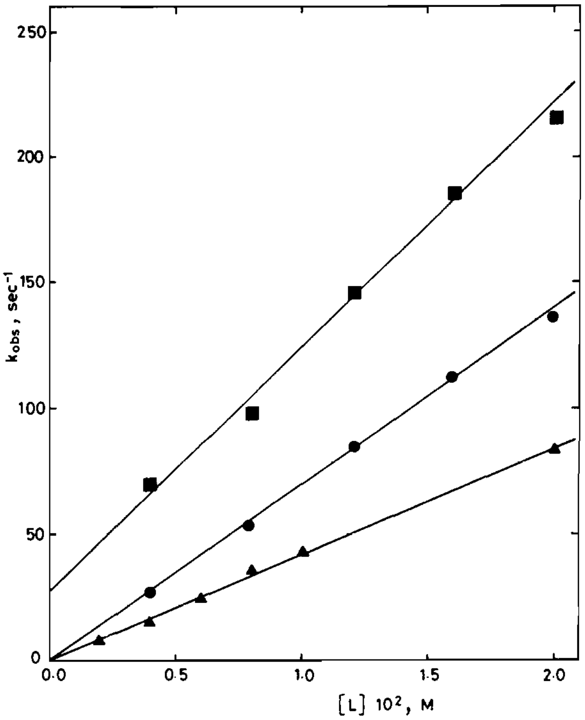

Fig. 1. Plot of k_1 *vs.* [L] for the reactions of $CH_3Rh(DH)_2H_2O$ with (■) N_3^-, (●) thiourea, (▲) pyridine. Full lines are calculated from the least squares parameters of Table I.

$$CH_3Rh(DH)_2H_2O + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3Rh(DH)_2L + H_2O \qquad (1)$$

$CH_3Rh(DH)_2H_2O$ was prepared as previously reported [11]. The reactions were followed spectrophotometrically by means of stopped-flow technique at 20 ± 0.2 °C, in water maintained at 1.0 *M* ionic strength with $NaNO_3$. The reactions were carried out in presence of an at least tenfold excess of incoming ligand.

$CH_3Rh(DH)_2H_2O$ behaves as a weak acid. The pK_a for the deprotonation of axial water, determined by means of a spectrophotometric titration with NaOH, was 9.78 ± 0.04. In the kinetic measurements both the complex and the ligand solution were buffered at pH ≅ 8. At this pH value the complex is almost completely in the form of an aquocomplex. The k_{obs} values, obtained as slope of the linear plots of $\log(A_t - A_\infty)$ *vs.* time (where A_t is the optical absorbance at time t and A_∞ is the final absorbance), show a linear dependence on [L] in the range of concentrations examined (Fig. 1), according to the expression:

$$k_{obs} = k_1[L] + k_{-1} \qquad (2)$$

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

TABLE I. Rate Constants for the Reactions $CH_3Rh(DH)_2H_2O + L \rightleftarrows CH_3Rh(DH)_2L + H_2O$, at 20 ± 0.2 °C, I = 1 *M* ($NaNO_3$), pH ≃ 8.

L	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	[L] range (*M*)
N_3^-	$(9.59 \pm 0.28) \times 10^3$	27.2 ± 3.6	$4.10^{-3}-2 \times 10^{-2}$
SCN^-	$(6.76 \pm 0.13) \times 10^3$	4.36 ± 0.95	$2 \times 10^{-3}-2 \times 10^{-2}$
I^-	$(4.66 \pm 0.18) \times 10^3$	32.0 ± 2.5	$4 \times 10^{-3}-2 \times 10^{-2}$
Pyridine	$(4.23 \pm 0.06) \times 10^3$		$2 \times 10^{-3}-2 \times 10^{-2}$
Thiourea	$(7.00 \pm 0.13) \times 10^3$		$4 \times 10^{-3}-2 \times 10^{-2}$

TABLE II. Rate Constants for the Reactions of $CH_3Rh(DH)_2H_2O$ with Thiourea at Various Temperatures.

t (°C)	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})
17°2	$(5.75 \pm 0.09) \times 10^3$	
20°4	$(7.00 \pm 0.13) \times 10^3$	
25°2	$(8.55 \pm 0.17) \times 10^3$	3.31 ± 1.09
29°6	$(11.55 \pm 0.11) \times 10^3$	4.72 ± 0.52
34°8	$(13.40 \pm 0.35) \times 10^3$	5.09 ± 1.58

$\Delta H^* = 7.74 \pm 0.32$ kcal/mol

$\Delta S^* = -14.57 \pm 1.06$ e.u.

Values of k_1 and k_{-1}, calculated by a linear least squares analysis, are summarized in Table I together with the range of concentration of L.

For the reactions with thiourea the k_1 values were determined at various temperatures (Table II). The activation parameters ΔH^* and ΔS^* were calculated by fitting the k_1–T data of the Eyring equation in the exponential form, as previously reported [6].

It appears from data of Table I that the substitution reactions of $CH_3Rh(DH)_2H_2O$ are very fast, about 100 times faster than the corresponding reactions of $CH_3Co(DH)_2H_2O$ [4]. This is a surprising feature, as generally the Rh(III) complexes are more inert than the Co(III) complexes (see above).

From the ratio of the rate constants for the water substitution reactions of $CH_3Rh(DH)_2H_2O$ and $Rh(TPPS)(H_2O)_2^{3-}$ (about 10^5) it may be deduced that a methyl group in a trans position has a more pronounced labilizing effect than that of a porphinic ring. The reactivity of the Co(III) complex derivatives with unsaturated macrocycles is very similar to that of the organometallic complexes [2–5].

The comparison of the activation parameters for the water substitution reactions with thiourea of $CH_3Rh(DH)_2H_2O$ (ΔH^* = 7.74 kcal/mol, ΔS^* = −14.57 e.u.) with those of $CH_3Co(DH)_2H_2O$ (ΔH^* = 14.62 kcal/mol, ΔS^* = 0.21 e.u. [6]) clearly indicates that the higher lability of the rhodium complex is due to the lower ΔH^* value. This lower ΔH^* value cannot be attributed to the weakening of the Rh–H_2O bond in the ground state. On the contrary, as the acid strength of an aquocomplex may afford an indirect estimate of the metal–oxygen bond strength [1], the pK_a values for the deprotonation of axial water (9.78 for $CH_3Rh(DH)_2H_2O$, 12.68 for $CH_3Co(DH)_2H_2O$ [12]) suggest a stronger metal–oxygen bond in the rhodium derivative. Hence the lower ΔH^* value arises from a stabilization of the transition state.

The k_1 values are practically independent of the nature of the incoming ligand (Table I). This suggests a dissociative activation process. On the other hand, the large negative value of the activation entropy suggests that an associative activation might occur in these reactions. It may be concluded that for the Rh(III) complexes bond making is more important and bond breaking less important than for the Co(III) complexes. In this hypothesis the low activation enthalpy may derive from partial compensation between the energetic cost of the bond breaking and the energy of the bong being formed.

Additional studies, including the relative effect of various alkyl groups σ bonded to the Rh(III) atom, are planned to elucidate the reaction mechanism for these complexes.

References

1 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, New York, N.Y. (1967).

2 K. R. Ashley and J. G. Leipoldt, *Inorg. Chem., 20,* 2326 (1981) and references therein.

3 G. Tauzher, R. Dreos Garlatti and G. Costa, *Inorg. Chim. Acta, 75,* 145 (1983).

4 A. L. Crumbliss and W. K. Wilmarth, *J. Am. Chem. Soc., 92,* 2593 (1970).

5 G. Tauzher, R. Dreos Garlatti, G. Costa and M. Green, *J. Chem. Soc. Chem. Comm.,* 413 (1973).

6 R. Dreos Garlatti, G. Tauzher, G. Costa and M. Green, *Inorg. Chim. Acta, 50,* 95 (1981).

7 J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta, 11,* 47 (1974).

8 K. R. Ashley, S. B. Shyu and J. G. Leipoldt, *Inorg. Chem., 19,* 1613 (1980).

9 M. Krishnamurty, *Inorg. Chim. Acta, 25,* 215 (1977).

10 F. Monacelli, *Inorg. Chim. Acta, 2,* 263 (1968).

11 J. H. Espenson and R. C. McHatton, *Inorg. Chem., 20,* 3090 (1981).

12 K. L. Brown, D. Lyles, M. Pencovici and R. G. Kallen, *J. Am. Chem. Soc., 97,* 7338 (1975).