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Mechanistic Studies on Rhodium(III) Chelates. Aquation of *Cis*-Dihalobisbiguaniderhodium(III) Nitrates

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Aquation of cis-*dihalobisbiguaniderhodium(III) nitrate for different halide ligands was investigated conductometrically. Rates of release of the first and second halide ions were derived by a graphical method. Activation parameters were calculated from Eyring equation and for chloro-, bromo-, and iodo-complexes* $\Delta H^{\ddagger}$ *values for the 1st step of aquation are 14, 15.1 and 17.4 kcal* mol^{-1} *and* $\Delta S^{\ddagger}$ *are* −25, −21.8 *and* −14.8 *e.u. respectively and for the 2nd step* $\Delta H^{\ddagger}$ *values are 12.3, 13.9 and 15.3 kcal* mol^{-1} *and* $\Delta S^{\ddagger}$ *are* −34.4, −32.6 *and* −27 *e.u. respectively. For the 1st step of aquation, metal–halide bond rupture is the only important factor and is virtually complete in the transition state. For the second step of aquation, bond formation by the 'aquo' ligand occurs before the bond rupture is complete. The loss of second halide ion takes place along with a hydrogen ion from the 'aquo' ligand with the resultant formation of hydroxoaquobisbiguanide complex.*

Introduction

The literature contains numerous descriptions of the aquation of rhodium(III) complexes. Long ago, Lamb [1] studied the aquation of the chloro– and bromo–pentammine complexes and recently studies on the sulphato- [2] and nitrato- [3] complexes have been reported. Other studies of aquation were made on dichloro–diamines [4, 5], mixed dihalo–diamines [6], and on hexachloro- [7(i)] and chloroaquo [7(ii)(iii)] complexes of rhodium(III). All these complexes aquate primarily by a 'dissociative mechanism' though there may also be some associative character. In order to have a proper idea about the aquation of rhodium–amine complexes, it will be better not only to have a change in the 'amine' ligand but also to have a change in the ligand to be displaced. With this idea, the present investigation was undertaken to study the aquation of $Rh(BigH)_2X_2^+$, where 'BigH' = 'biguanide' and X = Cl^-, Br^- and I^-. The gradual transition in the physical and chemical properties of the displaced ligand of similar nature may reveal interesting results. This will not only add to the general understanding of Rh(III)–amine reactions but would also contribute to the understanding of the aquation of biguanide complexes.

Experimental

Preparation of Complexes

Dichlorobisbiguaniderhodium(III) nitrate tetrahydrate, $[Rh(BigH)_2Cl_2]NO_3\cdot 4H_2O$

This was prepared by the method of Ghosh and Bhattacharya [8]. Found : N, 30.00; Cl, 14.33. Calcd. N, 30.20; Cl, 13.92%.

Dibromobisbiguaniderhodium(III) nitrate tetrahydrate, $[Rh(BigH)_2Br_2]NO_3\cdot 4H_2O$

The bromo–bromide complex $[Rh(BigH)_2Br_2]Br$ was first prepared [8] and the bromo–nitrate complex was obtained by metathesis of the bromo complex with silver nitrate. After removal of the silver bromide and on concentration of the filtrate, the product separated as yellow crystals. Found: N, 25.34; Br, 26.23. Calcd. N, 25.63; Br, 26.7%.

Diiodobisbiguaniderhodium(III) nitrate tetrahydrate, $[Rh(BigH)_2I_2]NO_3\cdot 4H_2O$

The iodo–iodide complex $[Rh(BigH)_2I_2]I$, was prepared [8] and the corresponding iodo–nitrate was obtained from this complex in a similar manner as above. Found: N, 22.32; I, 35.71. Calcd. N, 22.15; I, 36.65%.

Distilled water, redistilled in an all-glass still with potassium permanganate and alkali, was used for making all the solutions which were stored in Jena glass bottles.

All these complexes aquate in aqueous solution by successive release of halide ions and the course of aquation may be determined by measuring the change in conductance, which is the reciprocal of measured resistance, of the experimental solution. Measurements of resistance were made with a Philips conductivity bridge (Philips PR 9500/90) at the

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desired time interval with a dip-type cell which was thermostated at the desired temperature. Kinetic runs were carried out with freshly prepared aqueous solutions (the water for making the solutions being previously thermostated at the desired temperature) of the experimental complex in a well closed polypropylene vessel. The entire process of dissolution of the complex to the first recording of resistance takes about three minutes.

Results and Discussion

The amount of X^- released during the reaction, measured as AgX, indicates that the reaction proceeds almost completely in the forward direction forming $Rh(BigH)_2(H_2O)_2^{3+}$. The reaction does not follow simple first order kinetics. Therefore, it was assumed that the reaction occurs in a stepwise manner. The aquation of the diacidocomplex may then be represented as:

$$\underset{\text{I}}{[Rh(BigH)_2X_2]NO_3} + H_2O \xrightarrow{k_1} \underset{\text{II}}{[Rh(BigH)_2(H_2O)X]NO_3{\cdot}X} \qquad (1)$$

and

$$\underset{\text{II}}{[Rh(BigH)_2(H_2O)X]NO_3{\cdot}X} + H_2O \xrightarrow{k_2} \underset{\text{III}}{[Rh(BigH)_2(H_2O)_2]NO_3{\cdot}X_2} \qquad (2)$$

The values of k_1 and k_2 were derived graphically from the observed variation in the conductance of the solution with time, by a method similar to that used in the determinations of half-lives of two radioactive parent–daughter components when there is no equilibrium [9], and applied in the kinetic study by Ashley and Hamm of the formation and aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ [10]. Instead of absorptivities, in this study conductivities of different species have been considered.

Let C_o, C_t and C_∞ be the conductance values of the solution under identical conditions at 'zero' time, time 't' and 'infinite' time respectively; then,

$$\alpha C_t = \Lambda_1[I] + \Lambda_2[II] + \Lambda_3[III] \qquad (3)$$

and

$$I_o = [I] + [II] + [III] \qquad (4)$$

where 'α' is the cell constant and I_o is the initial concentration of the complex taken, [I], [II] and [III] are the molar concentrations of the species $[Rh(BigH)_2X_2]NO_3$, $[Rh(BigH)_2(H_2O)X]NO_3{\cdot}X$ and $[Rh(BigH_2(H_2O)_2]NO_3{\cdot}X_2$ respectively at any stage of the reaction at time t, while Λ stands for the molar conductance of the species indicated as its subscript at the experimental temperature. From equations (3), (4) and standard equations of consecutive reactions [11], the following equation may be derived

$$(C_\infty - C_t) = a_1 e^{-k_1 t} + a_2 e^{-k_2 t} \qquad (5)$$

where k_1 and k_2 are the rate constants for the release of first and second halide ions and a_1 and a_2 are two

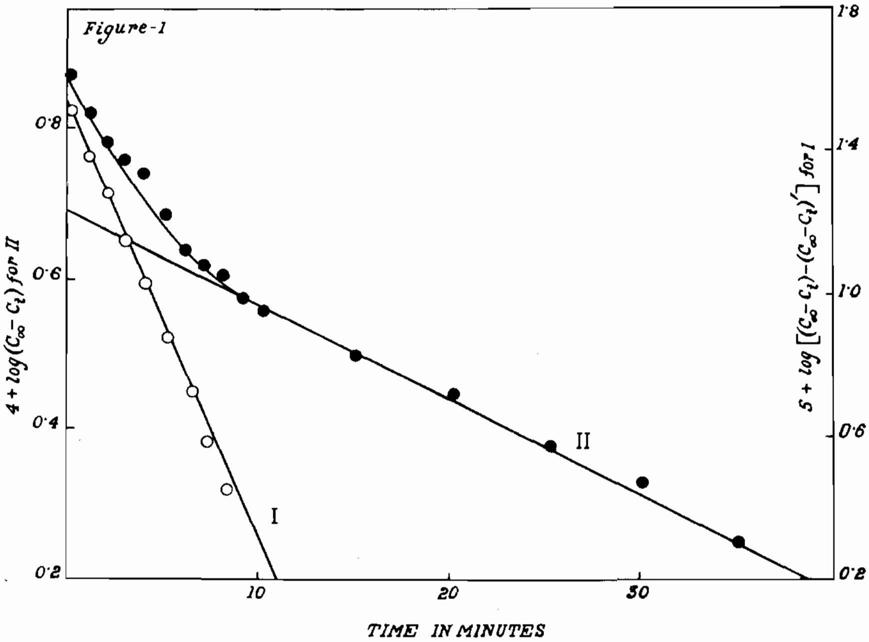

Figure 1. Aquation of *cis*-dichlorobisbiguaniderhodium(III) nitrate complex. 0.002 *M*, temperature 40 °C. I, First (fast) step of aquation; II, Second (slow) step of aquation.

constants composed of rate constants, molar conductivities and the cell constant. Figure 1 shows a typical rate plot of $\log(C_\infty - C_t)$ *vs.* time 't' for a $2 \times 10^{-3} M$ solution of the complex $[Rh(BigH)_2Cl_2]NO_3$ at 40 °C. The rate constants k_2 and k_1 are obtained respectively from the slopes of (i) the straight line segment of the graph at longer times and (ii) the straight line obtained by plotting $\log[(C_\infty - C_t) - (C_\infty - C_t)']$ *vs.* time, where $(C_\infty - C_t)'$ denotes the extrapolated $(C_\infty - C_t)$ value to time 'zero'.

TABLE I. Rate Constants for the First (k_1) and Second (k_2) Stages of Aquation at Different Temperatures.

Complex		Temperature, °C			
		32	40	45	50
$Rh(BigH)_2Cl_2^+$,	$10^3 k_1$, sec^{-1}	2.40	5.10		9.24
	$10^4 k_2$, sec^{-1}	3.65	5.29		10.10
$Rh(BigH)_2Br_2^+$,	$10^3 k_1$, sec^{-1}		2.76	3.95	6.00
	$10^4 k_2$, sec^{-1}		4.03	5.57	7.67
$Rh(BigH)_2I_2^+$,	$10^3 k_1$, sec^{-1}		3.29	5.10	8.10
	$10^4 k_2$, sec^{-1}		3.68	4.83	7.30

The rate constants thus obtained for all the complexes at various temperatures are listed in Table I. Duplicate runs were made for each rate plot and the deviations were found to be within 3 percent. It is interesting to note that in the temperature range 30°–50 °C, the rate sequence for the first stage of aquation is $Cl^- > I^- > Br^-$, which is the general trend observed in the acid [1] and base [12] hydrolysis of rhodium(III) pentammine complexes.

TABLE II. Activation Parameters for the Aquation of Rhodium(III) Biguanide Complexes (see text).

Complex	$\Delta H^\ddagger$ kcal mol^{-1}	$\Delta S^\ddagger$ e.u.	$\Delta S_{hydration}$	
			X^-	HX
$Rh(BigH)_2Cl_2^+$	14	−25	−23.1	
$Rh(BigH)_2Br_2^+$	15.1	−21.8	−19.2	
$Rh(BigH)_2I_2^+$	17.4	−14.8	−14.8	
$Rh(BigH)_2(H_2O)Cl^{2+}$	12.3	−34.4		−31.1
$Rh(BigH)_2(H_2O)Br^{2+}$	13.9	−32.6		−27.8
$Rh(BigH)_2(H_2O)I^{2+}$	15.3	−27		−22.7

Table II records the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of all the complexes as obtained from an Eyring plot [13], errors in the estimation of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ being *ca.* ± 1 kcal mol^{-1} and ± 3 e.u. respectively. The $\Delta S^\ddagger$ values of the aquation of dihalo- complexes (equation 1) are nearly equal to the ΔS values of the hydration of respective halide ions [14]. $\Delta S_{hydration}$ of all the halides, except fluoride, and their hydracids have been included in Table II for the convenience of comparison. The nearly equal ΔS values for the three halo complexes suggest that the aquation of dihalo-complexes occurs by a dissociative process in which 'bond breakage' (Rh–X) is only important and is virtually complete in the transition state.

The plots of $\Delta S^\ddagger$ for dihalo- and aquohalo- complexes *vs.* the entropy of hydration of respective halide ions give straight lines in each case with slopes nearly equal to 1.0 and 0.9. The observed little deviation of the slope of the first line from unity seems to be due to the error in the estimation of $\Delta S^\ddagger$. This indicates that for the dihalo- complex, the dissociation is virtually complete in the transition state, but for the aquohalo- complex, the fractional value of the slope indicates that the halide ion is weakly bound to the metal atom in the transition state along with the incoming 'aquo' ligand. $\Delta S^\ddagger$ values for aquohalo- complexes are more negative than $\Delta S_{hydration}$ of the respective halide ions and are very close to the hydration entropies of the respective halogen hydracids [15].

In aqueous solution, the diaquo- complex $Rh(BigH)_2(H_2O)_2^{3+}$, like all other diaquobisbiguanide complexes [16], most probably exists in hydroxo-aquo form with the liberation of a hydrogen ion from one of the aquo ligands. The great tendency to formation of the hydroxoaquo- complex over the diaquo- complex in the second step of aquation probably takes place with release of a hydrogen ion (H^+) alongwith X^-. This might explain the observed $\Delta S^\ddagger$ value for the second step of aquation which is nearly equal to the entropy of hydration of the respective hydracids. Actual release of H^+ takes place during the aquation and this has been observed by a decrease in pH of the experimental solution, *viz.* from that of water (*ca.* 6.0) to *ca.* 3.0 at the end of the aquation. Use of isotopic H^+ in the form of $[Rh(BigH)_2(D_2O)X]^{2+}$ would have been the best guide for such a mechanism, but could not be applied at present due to unavoidable reasons. The second step of aquation, as given in equation (2), is then probably better represented by:

$$[Rh(BigH)_2(H_2O)X]NO_3 \cdot X + H_2O \xrightarrow{k_2} [Rh(BigH)_2(OH)(H_2O)]NO_3 \cdot X + HX$$

In equation (3), [III] should stand for the molar concentrations of the species $[Rh(BigH)_2(OH)(H_2O)]NO_3 \cdot X$ and HX and Λ_3 for their combined molar conductance.

Biguanide, with its six-membered chelate ring of quasi-aromatic character [17] should result in the formation of more stable complex than with ethylenediamine (en). But the inductive effect of the strongly basic ligand 'BigH' makes the 'metal' atom apparently more negative, with higher rate for the release of a negative X^- ion. This is apparent from the rate of the release of the first chloride ion in the two dichloro- complexes as shown below:

Temp.	Complex	pk_1 of the chelate ligand at 25 °C	10^4k sec^{-1}	
80°	*Cis*-$Rhen_2Cl_2^+$	9.93	8.5	Ref. 4
80°	*Cis*-$Rh(BigH)_2Cl_2^+$	12.8	*ca.* 700	(extrapolated value obtd. from Eyring plot)

When the rate constant for the aquation of $Rh(BigH)_2Cl_2^+$ is compared with that of $Co(BigH)_2Cl_2^+$, it can be seen that the rhodium complex reacts substantially at a slower rate than the corresponding cobalt species (the cobalt complex is extremely reactive in aqueous solution, and complete dissociation of coordinated halide ions takes place by the time of dissolution [16]). This is in agreement with the results found for other rhodium(III) and cobalt(III) complexes [4].

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