

Kinetics & Mechanism of Acid-catalysed Dissociation of Tris(1-amidino-O-alkylurea)cobalt(III) Complexes

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Received 19 November 1981; revised and accepted 26 December 1981

Kinetics of acid-catalysed dissociation of three tris(1-amidino-O-alkylurea)cobalt (III) complexes (alkyl groups being methyl, ethyl and *n*-butyl respectively) have been investigated spectrophotometrically between 64° and 78°C in the presence of 0.7 to 2.0 *M* perchloric acid. The dissociation proceeds only through acid-dependent path and follows a conjugate-acid mechanism. The rate constants primarily depend on the basicity of the ligands. Substitution of different alkyl groups on the side chain seems to have little effect on the rate. Activation parameters for the reactions have been evaluated.

As a part of a broad programme on the reactions of six-membered chelate complexes¹⁻³, we have presently undertaken the study of the acid-catalysed dissociation of tris(1-amidino-O-alkylurea)cobalt(III) complexes. Reactions of six-membered chelate complexes differ from those of five-membered complexes in many ways and various substitutions on the ring indicate some interesting results^{3,4}. In the present series of complexes, the alkyl substitutions are on the side chain instead of on the ring. The alkyl substitution increases the size of the chain without adding much strain to the ring. With different alkyl substitutions, the basicity of the ligand also changes. Our object is also to find out the effect of these factors on the rate of dissociation of these complexes.

Materials and Methods

All the reagents used were of either reagent grade quality or were purified by suitable methods. Doubly distilled water was used for preparing all the solutions.

Tris-1-amidino-O-methylureacobalt(III), *tris-1-amidino-O-ethylureacobalt(III)* and *tris-1-amidino-O-(n)butylureacobalt(III) perchlorates* [abbreviated as Co(AMUH)₃(ClO₄)₃, Co(AEUH)₃(ClO₄)₃ and Co(ABUH)₃(ClO₄)₃ respectively]. Corresponding sulphates of these complexes were prepared by the method of Dutta *et al.*^{5,7}. The perchlorate salts were prepared, in solution, whenever required by the metathesis of sulphate complex with barium perchlorate. The analytical data of the sulphate complexes are given in Table 1.

Absorption spectra of the complexes at different acidities — The absorption spectra of each of the complexes in their protonated or deprotonated form were identical, exhibiting maximum absorption at 476 nm (see Fig. 1). The spectra of a series of solutions of each of these complexes (3 × 10⁻³ *M*) containing different amounts of acid (HClO₄) varying

TABLE 1 — ANALYTICAL DATA OF THE SULPHATE COMPLEXES

Complex	Found (calc.)%		
	N	Co	SO ₄
Co(C ₂ N ₄ H ₆ O.CH ₃) ₃ .(SO ₄) _{1.5} .4H ₂ O	27.89 (27.41)	10.0 (9.62)	23.72 (23.49)
Co(C ₂ N ₄ H ₆ O.C ₂ H ₅) ₃ .(SO ₄) _{1.5} .5H ₂ O	24.73 (24.60)	9.01 (8.64)	20.75 (21.09)
Co(C ₂ N ₄ H ₆ O.C ₄ H ₉) ₃ .(SO ₄) _{1.5} .1.5H ₂ O	24.02 (23.86)	8.63 (8.38)	20.58 (20.45)

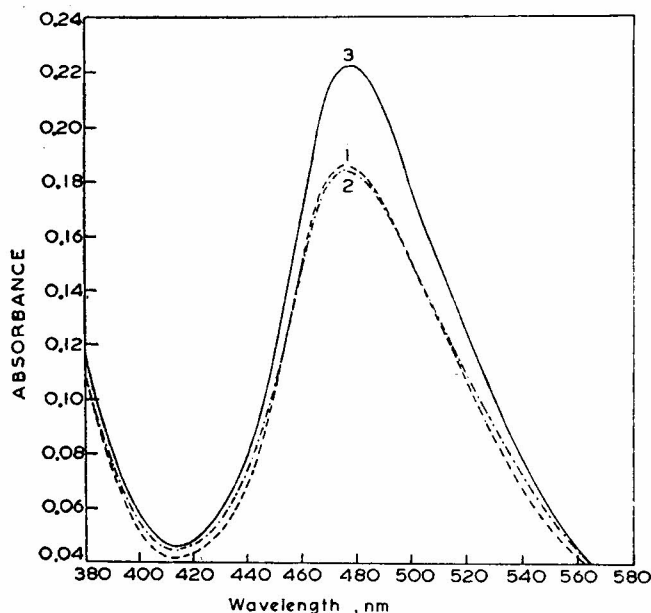


Fig. 1 — Absorption spectra of complexes [(1) methyl complex (2) ethyl complex (3) *n*-butyl complex (1 × 10⁻³ *M* aqueous solutions)]

from 0 to 2.0M were recorded on an ECIL spectrophotometer, immediately after preparation and after 2, 4, 6 hr, 1, 2, 3, days up to two weeks in the temperature range 30° to 80°C. The spectra of all the solutions practically remained unchanged below 50° and only above 60° and in the presence of 0.5 M or higher acid concentrations, fairly well measurable rates were observed. In this range of temperature, the spectra of the solutions do show a little change after a day, indicating the formation of the diaquo bis-complexes.

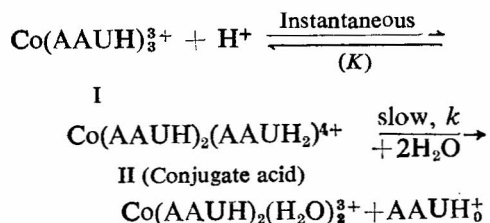
Kinetic runs — These were carried out in stoppered Jena volumetric flasks, at the desired temperature maintained with an accuracy of $\pm 0.1^\circ\text{C}$. Aliquots (3 ml each) of the reaction mixture were withdrawn at regular time intervals, quenched by putting in a test tube dipped in cold-water around 5° and the absorbance measured immediately.

The pseudo-unimolecular rate constants for all these complexes were evaluated by Guggenheims method⁸ as it was difficult to ascertain the absorption due to pure bis-complexes.

Results and Discussion

The rate constants obtained at various acid concentrations and temperatures but at constant ionic concentration ($I = 2.0 M$), are given in Table 2. Duplicate readings were recorded for all the rate constant values. Deviations in the observed rate values were within 2 to 3%. The observed pseudo-first order rate constants (k_{obs}) for all the complexes are independent of [complex], but dependent on [acid]. The plots of k_{obs} versus [acid] for each of the complexes at different temperatures are linear, showing first order dependence of rate on [acid]. These plots make zero intercept on the rate axis, showing that the aquation of all the three complexes proceed through acid-dependent paths only, as observed with similarly constituted tris-biguandecobalt(III) complexes⁹.

For all the complexes, the mechanism of aquation may be represented as shown in Scheme 1.



('AAUH' stands for methyl, ethyl or butyl substituted ligands)

Scheme 1

On the basis of the mechanism given in Scheme 1, the rate of dissociation of any of these complexes may be represented by Eq. (1)

$$\begin{aligned} \text{Rate} &= k[\text{Conjugate acid}] = kK[\text{Complex}][\text{H}^+] \\ &= k^*[\text{Complex}][\text{H}^+] \end{aligned} \quad \dots (1)$$

where k^* is the second order rate constant, K is the equilibrium constant for the formation of the protonated species (conjugate acid) and k is the rate constant for the rate-determining step. K is assumed to be very small so that $[\text{I}] \gg [\text{II}]$.

The second-order rate constants for all the complexes were derived from the slopes of the plots of k_{obs} versus [acid]. The second-order rate constant values, given in Table 2, are accurate within 3–4%. Activation parameters as calculated from Eyring equation¹⁰ are given in Table 3.

The basicity of the ligand, which determines the formation of the protonated intermediate and the stability of the complex, which depends on the size and the number of substituted groups on the chelate ring, are the two main factors which control the rate of dissociation of these complexes. The protonated transitory intermediate is formed by the protonation of the ligand at its basic site (imino group). Acid dissociation constants of the ligands, as determined by Bjerrum technique, reveal that the basicities of the ligands increase in the order methyl < ethyl < butyl⁵. Although the basicities of the ligands

TABLE 2 — RATE DATA FOR THE ACID-CATALYZED DISSOCIATION OF TRIS (1-AMIDINO-O-ALKYLUREA)COBALT(III) COMPLEXES AT DIFFERENT ACIDITIES AND TEMPERATURES

[Complex] = $3 \times 10^{-3} M$; I = 2.0 M

Complex	Temp. °C	10 ⁴ k(sec ⁻¹) at HClO ₄ Conc. (M)						10 ⁴ k*
		0.7	1.0	1.25	1.5	1.75	2.0	
Co(AMUH) ₃ ³⁺	64	—	—	1.15	1.26	1.7	2.3	1.05
	70	—	1.7	—	2.30	—	3.26	1.60
	78	2.39	3.07	—	4.6	—	—	3.0
Co(AEUH) ₃ ³⁺	64	—	—	—	1.91	—	2.57	1.25
	70	—	2.78	—	3.45	—	4.79	2.35
	78	3.07	4.10	—	5.75	—	—	4.2
Co(ABUH) ₃ ³⁺	70	—	1.48	—	2.32	—	2.92	1.5
	78	—	3.7	—	6.03	—	—	3.8

TABLE 3 — ACTIVATION PARAMETERS OF HYDROLYSIS OF THE COMPLEXES

Complex	ΔH^\ddagger kcal mol ⁻¹	ΔS^\ddagger kcal mol ⁻¹ deg ⁻¹
Co(AMUH) ₃ ³⁺	17.0 ± 1.0	-41. ± 4
Co(AEUH) ₃ ³⁺	19.2 ± 1.1	-33.7 ± 4
Co(ABUH) ₃ ³⁺	28.5 ± 3.0	- 7.5 ± 9

change after coordination, it may be considered logically that the order remains the same. Greater basicity of a ligand would lead to a greater amount of the protonated intermediate complex, and a higher rate. This is well reflected from the rate pattern of the complexes. Biguanides, which are more basic than 1-amidino-O-alkylureas, form complexes, which dissociate at a much higher rate⁹. It may be observed from Table 2, that substitution may also have some influence on the rate of dissociation. Although at all temperatures rate does not increase consistently from methyl to butyl complex, but the enthalpy of the reaction increases considerably. When dissociation mechanism operates, a 'bulky' substitution on the chelate ring should promote the rate of hydrolysis and the ease of bond-rupture should be reflected from the lower enthalpy of the reaction. However, in the present series of complexes the enthalpy values increase consistently from methyl to butyl complexes. This opposite trend indicates that the substituent has probably no effect on the rate of dissociation of these complexes. So it is likely that the basicity of the ligand, which controls the formation of the intermediate, is the only factor which determines the rate of dissociation. In biguanide complexes also, it has been observed that only the basicities of the ligands control the rates of dissociation and the size of the substituent has little effect on the rate⁹.

Highly negative entropy values for the methyl and the ethyl urea complexes indicate that the dissociation of these two complexes follow a similar mechanism and the departure of the outgoing ligand is complete in the transition state. However, the entropy of butyl complex is less negative, the reason for which is not well understood.

Introduction of an alkyl (methyl or ethyl) substituent on the pseudo-aromatic biguanide ring in a rhodium(III) complex has been shown to increase the stability of the metal complex by hyperconjugation involving the pseudo-aromatic biguanide ring and the alkyl substituent. A corresponding decrease in the rate of dissociation has also been noticed for these complexes². However, in our complexes, although the six-membered 1-amidino-O-alkylurea chelate ring contains delocalised π -electrons, and the alkyl substitutions are not on the chelate ring, hyperconjugation cannot take place, and the rates of dissociation of the complexes remain unaffected. Insensitivity of the rate towards various substituents again establishes the structure of these complexes, as proposed by Dutta and Syamal⁷; the substituents are on a side chain through oxygen linkage, instead of on the ring itself, as proposed earlier by Dutta and Ray¹¹.

Acknowledgement

The authors express their sincere thanks to the authorities of the University of Kalyani and the CSIR, New Delhi for the award of research fellowships to (S.M.) and (B.N.).

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