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KINETIC PARAMETERS AND SOLID STATE MECHANISM IN INORGANIC COORDINATION COMPOUNDS

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ABSTRACT

A thermal and kinetic study of the anation-dehydration reaction of amine complexes of Co(III), Cr(III), Rh(III) and Ir(III) containing entering anions of type halo- and ciano- complexes has been carried out with isothermal and dynamic TG. The thermodinamic and kinetic parameters have been calculated using the different physical models proposed. Several of the compounds studied show disagreement with House theory, a fact which leads us to propose a greater contribution of the anion-cation volume ratio ("free space theory") compared with the Crystal Field Activation Energy (C.F.A.E.).

INTRODUCTION

The solid phase deaquation-anation of aquoamminemetal(III) salts (M(III)= Co(III) or Cr(III), has been widely studied. For example, the reaction:
$[Co(H_2O)(NH_3)_5]X_3 \longrightarrow [Co(X)(NH_3)_5]X_2 + H_2O$
has been examined by several research groups since 1959, notably by Wendlandt and co-workers (1). The activation energies for these reactions are reported to vary with the anion. Variations in activation parameters with the nature of anion are also reported for the deaquation-anation of $[Cr(H_2O)(NH_3)_5]X_3$ (2) and $[Ru(H_2O)(NH_3)_5]X_3$ (3). In a very interesting paper, J.E. House (4) proposed a general mechanism for these reactions in which the generation of a point defect is considered as the formation of the transition state. The two types of point defects considered are analogous to the Schottky or Frenkel types occurring in simple crystals. These dehydration reactions are more consistent with the formation of a Frenkel type defect and a S_N1 (dissociative) mechanism Later, LeMay (5) reinterpreted and satisfactorily compared this theory with the literature data; in the same field we have found that the dehydration-anation mechanism of several aquoamine complexes of chromium (III) and cobalt (III) with cyanocomplexes as entering ligand is always consistent with a dissociative mechanism.

If the process takes place by S_N1 pathway, the rate determining step is the loss of the water and the activation energy should be almost invariant, with the nature of the anion, provided that the structure of the complexes is very similar. Furthermore, the principal contribution to E_a must be, according to House(4), the Dq factor of M(III) (due to passing from hexacoordination to the square pyramid intermediate). However, our previous results on ammine complexes of rhodium and iridium(III) are inconsistent with the mean contribution of Crystal Field Activation Energy (C.F.A.E.) derived from the Dq values (6). In this work we present the results obtained on several aquoamines of Cr(III), Co(III), Rh(III) and Ir(III) and we indicate that for the second and third series of transition, the Basolo and House C.F.A.E. is inconsistent with the experimental results. We propose that the determining step is the "free space" in the crystal lattice, as determined by the cation-anion ratio.

SYNTHESIS

All the series of complexes used in this work have been synthesized by the present authors (see references in Table II).

EXPERIMENTAL

Thermogravimetric studies were carried out on a Perkin-Elmer TGS-I system in a nitrogen atmosphere. Non-isothermal measurements were made at a rate of 5°/min^{-1} with 5-7 mg. samples. The kinetic parameters were determined on the

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basis of the general kinetic relation

$$d\alpha / dt = K(T)\, f(\alpha)$$

where $K(T) = K_o \exp(-E_a/RT)$ (Arrhenius law); K = frecuency factor; E_a = activation energy and α = mole fraction. Mathematically, this expression can be converted to

$$\int_0^1 d\alpha/f(\alpha) = \int_{T_0}^{T_1} K(T)\, dt \quad \text{being} \quad \int_0^1 d\alpha\, /f(\alpha) = g(\alpha)$$

TABLE 1

Kinetic functions, $g(\alpha)$, used in their integral form

Mechanism	$g(\alpha)$
Nucleation controlled	
Exponential law	$\ln \alpha^n$
Power Law	$\alpha^{1/n}$
Growth controlled	
General	$\|1-(1-\alpha)^{1-n}\|/(1-n)$
for n = 1	$\|-\ln(1-\alpha)$
Nucleation-Growth controlled	
Avrami-Erofeev	$\|-\ln(1-\alpha\|^{1/n}$
Prout-Tompkins	$\ln\|\alpha/(1-\alpha)\|$
Diffusion controlled	
One-dimensional	α^2
two-dimensional	$\alpha+(1-\alpha)\ln(1-\alpha)$
three-dimensional	$\|1-(1-\alpha)^{1/3}\|^2$
three-dimensional	$(1-2/3\alpha) - (1-\alpha)^{2/3}$

The main difficulty in solid kinetics is to find the appropriate expression for $g(\alpha)$ and $f(\alpha)$.

In this work we have used all the principal expressions of $g(\alpha)$ (15) given in the literature (table 1), which follow the four physical models of solid-state chemistry: nucleation, growth, nucleation-growth, and diffusion. The true activation energy was determined by a series of isothermal TG curves which gave a value of E_a almost independent of the physical model proposed. To find the more likely solid-state model this value has been compared with the variable values obtained with non-isothermal measurements. In non-isothermal measurements the expression $g(\alpha) = K(T)dt$ was resolved by the widely employed approximation of Coats and Redfern (16). For isothermal analysis the general equation is simply $g(\alpha) = Kt$. In this case, an isothermal preheating at low temperature (50-60°C) to constant weight was made to eliminate the external water. All the calculations were made with a Fortran IV program.

Table II gives the values found of E_a for 31 aquacomplexes of Co, Rh, Ir, and Cr containing amines and anions of different size: en(ethylenediamine), tmd(1,3-diaminopropane); $|M(CN)_4|^{2-}$ (M = Ni, Pd, Pt); $|M(CN)_6|^{3-}$ (M = Co, Cr) and Cl^-, Br^- and I^-.

TABLE II

				(E_a= Kj/mol)		
	M:	Ni	Pd	Pt	CFAE	Ref.
$\|Co(NH_3)_5(H_2O)\|_2\|M(CN)_4\|_3$		115	124	67	100	(7)
$\|Rh(NH_3)_5(H_2O)\|_2\|M(CN)_4\|_3$		105	115	90	152	(8)
$\|Ir(NH_3)_5(H_2O)\|_2\|M(CN)_4\|_3$		107	118	91	180	(8)
$\|CrF(H_2O)(en)_2\|\|M(CN)_4\|$		132	140	111	100	(9)
$\|CrF(H_2O)(tmd)_2\|\|M(CN)_4\|$		103	108	88	100	(9)

X:	Cl	Br	I	CFAE	Ref.
$\|Ir(NH_3)_5(H_2O)\|X_3$	75	105	120	180	(10)
(aa'):	en	en-tmd	tmd		
$\|CrF(H_2O)(aa')_2\|I_2$	130	100	70	100	(11)
(aa'):	en	tmd			
$K\|CrF(H_2O)(aa')_2\|\|Cr(CN)_6$	118	86	- -	100	(12)
$K\|CrF(H_2O)(aa')_2\|\|CrNO(CN)_5\|$	96	80	- -	100	(12)
M':	Co	Pt	Ir		
$\|M'(NH_3)H_2O\|\|CrNO(CN)_5\|$	108(100)	126(152)	139(180)	- -	(13)
$\|M'(NH_3)H_2O\|\|Co(CN)_6\|$	127(100)	117(152)	88(180)	- -	(14)

a) Even when the values of the CFAE increase along the series Co(III), Rh(III), Ir(III) (right column), the values of E_a for Rh and Ir are similar and lower than for Co. Only for Co is there agreement with the CFAE of Basolo-House.

b) The complexes containing 1,3-diaminopropane (other ligands being equal) show values of E_a lower than with the less bulky ethylenediamine.

c) The results are very similar with similar entering anions, such as $|M(CN)_4|^{2-}$ (M = Ni, Pd); $|Cr(CN)_6|^{3-}$, $|CrNO(CN)_5|^{3-}$ and $|Co(CN)_6|^{3-}$.

d) E_a values for complexes containing the anion $|Pt(CN)_4|^{2-}$ are invariably lower than those with $|M(CN)_4|^{2-}$ (M = Ni, Pd); they are also lower than the expected CFAE.

e) For $|Ir(H_2O)(NH_3)_5|X_3$, different values of E_a (increasing in the order Cl, Br, I) are found.

DISCUSSION

All the above observations can be related to the larger or smaller volume that coordinated water has available to leave the lattice (i.e. free space). Therefore, lacking a quantitative study based on structure determinations (a work which is currently under way), the greater or lower packing ability of the ions seems to be the determining factor of the process; the greater this capacity, the lower likelihood for the water moelcule to leave the lattice and the greater values of E_a. This is shown by the size of the anions, by the size of the central atom and by the anion $|Pt(CN)_4|^{2-}$ whose Pt-Pt interactions in the solid phase leave more free space and lower the value of E_a.

House theory, based fundamentally on the concept of Dq and CFAE seems valid only for the first row transition metal complexes. Nevertheless, given that the E_a values found are lower than CFAE itself, we can propose a dissociative mechanism (S_N1) involving a square pyramid intermediate for the dehydration-anation reaction.

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