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Derivatographic Studies on Transition Metal Complexes. IV.[1] Deaquation-Olation of Hydroxoaquo Cobalt(III) Complexes with Aminotricarboxylic Acids.[2]

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Thermochemical functions of the deaquation-olation on $K[Co(OH)L_4(H_2O)]$ type complexes in the solid phase were determined by means of derivatography and UV spectral measurements and the mechanisms were discussed on the basis of the results. In the above formula, L_4, denotes nitrilotriacetate (nta), nitriloisopropionicdiacetate (nipda), *d,l*-α-amino-*n*-butyric-*N,N*-diacetate (α-abda), *l*-leucine-*N,N*-diacetate (*l*da), *l*-valine-*N,N*-diacetate (vda), *d*-α-phenylglycine-*N,N*-diacetate (pgda), or *d,l*-α-phenylalanine-*N,N*-diacetate (pada) ions. These complexes were found to liberate one mole of coordinating water upon heating and to turn into the olated compound bridged with two OH groups at the same time. From an estimation of enthalpy change and activation energy for the reaction, it was found that the reaction is apt to take place more easily as the structural complexities of chelating agents increase and that the reaction always proceeds in the first order. We might conclude that the evolution of coordinating water is the rate-determining step in the reaction.

In 1907, Werner found that when $[Co(OH)(H_2O)(NH_3)_4]X_2$ type complexes were heated at *ca.* 100°C, the following olation took place.[3]

$$2[Co(OH)(H_2O)(NH_3)_4]X_2 \longrightarrow [(NH_3)_4Co(OH)_2Co(NH_3)_4]X_4 + 2H_2O$$

Wendlandt and Fisher estimated the heats of olation in several complexes of the above type in which only the counter anions are different from each other.[4]

Pfeiffer observed that when the red $[Cr(OH)(H_2O)en_2]Cl_2$ is heated at 120°C, a bluish violet salt is formed.[5] He also suggested that the resulting salt has two bridged OH groups between two metal atoms and the reaction is expressed as follows:[6]

$$2[Cr(OH)(H_2O)en_2]Cl_2 \longrightarrow [en_2Cr(OH)_2Cr\ en_2]Cl_4 + 2H_2O$$

From the fact that the reaction of this type could occur readily, the red salt is considered to have the *cis* configuration with respect to the position of OH and H_2O.

In general, if the quadridentate ligands such as NTA or its analogues reside in the octahedral environment together with OH and H_2O, the latter two are situated at the *cis* position with each other. Therefore, this kind of complex is expected to bring about the olation expressed by

$$2K[M(OH)L_4(H_2O)] \longrightarrow K_2[L_4M(OH)_2ML_4] + 2H_2O.$$

It might be named "Deaquation-olation," because it involves both deaquation of the coordinating water and formation of the olated compound simultaneously. A few examples of such reactions have already been found on the cobalt(III) complexes with the aminotricarboxylic acids.[7—10] However, little thermochemical or kinetic functions of the reaction were reported and no mechanism discussed. Therefore, the present study was undertaken (1) to trace the thermal reaction by means of derivatography, (2) to estimate the enthalpy change (ΔH) and activation energy (E^{*}) of the respective thermal reactions, and (3) to deduce the mechanisms of the reaction.

TABLE 1. STRUCTURES AND ABBREVIATIONS OF THE CHELATING AGENTS AND THE COMPLEXES THEREWITH

Rational formula	R	Abbreviation[a]	Complex
	-H	NTA	$K[Co(OH)nta(H_2O)]\cdot H_2O$[7] (I)
R	$-CH_3$	NIPDA	$K[Co(OH)nipda(H_2O)]\cdot 2H_2O$[8] (II)
|	$-C_2H_5$	α-ABDA	$K[Co(OH)\alpha\text{-}abda(H_2O)]\cdot 2H_2O$[10] (III)
╱CHCOOH	$-CH(CH_3)_2$	VDA	$K[Co(OH)vda(H_2O)]\cdot 1.5H_2O$[10] (IV)
N—CH_2COOH	$-CH_2\cdot CH(CH_3)_2$	LDA	$K[Co(OH)\,l\text{da}(H_2O)]\cdot H_2O$[9] (V)
╲CH_2COOH	$-C_6H_5$	PGDA	$K[Co(OH)pgda(H_2O)]$[10] (VI)
	$-CH_2\cdot C_6H_5$	PADA	$K[Co(OH)pada(H_2O)]\cdot 5H_2O$[10] (VII)

a) NTA: Nitrilotriacetic acid
NIPDA: Nitriloisopropionicdiacetic acid
α-ABDA: *d, l*-α-Amino-*n*-butyric-*N,N*-diacetic acid
VDA: *l*-Valine-*N,N*-diacetic acid
LDA: *l*-Leucine-*N,N*-diacetic acid
PGDA: *d*-α-Phenylglycine-*N,N*-diacetic acid
PADA: *d,l*-α-Phenylalanine-*N,N*-diacetic acid

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[1] Part III of this series: R. Tsuchiya, K. Murai, A. Uehara, and E. Kyuno, This Bulletin, **43**, 1383 (1970).

[2] Presented at the 23rd Annual Meeting of the Chemical Scoiety of Japan, Tokyo, April, 1970.

[3] A. Werner, *Ber.*, **40**, 4434 (1907).

[4] W. W. Wendlandt and J. K. Fisher, *J. Inorg. Nucl. Chem.*, **24**, 1685 (1962).

[5] H. Pfeiffer, *Z. Anorg. Allg. Chem.*, **56**, 261 (1907).

[6] H. Pfeiffer, *ibid.*, **29**, 107 (1901).

Experimental

Preparation of Starting Complexes. Table 1 gives the rational formulas of the ligands and the chemical formulas of the complexes containing the ligands in the present work. All the ligands are analogues of NTA, and they can form the complexes including the 5,5,5-membered chelate rings when they act as a quadridentate ligand. The complexes were prepared by the methods described in respective references.[7–10]

Derivatographic Measurement. The derivatograms for these complexes were obtained with a Metrimpex Derivatograph Typ-OD-102. All the measurements were carried out in a constant nitrogen stream under the heating rate of 1°C min^{-1}. Five-hundred milligrams of the sample was used in each run. Analysis of derivatograms for each reaction process was carried out in a similar way to that described in part I of this series.[11]

Measurement of Electronic Spectra. The electronic spectra of the complexes were measured with a Hitachi EPU-2A Spectrophotometer in solid state by means of a diffuse-reflection method.

Results and Discussion

Observation on the Thermal Reaction Process by Derivatography. Figure 1 contains the derivatograms for nta- (I), nipda- (II) and *l*da-compleses (V) as the representatives. As seen in this figure, complex II liberates successively two moles and one mole of water at about 100 and 195°C, respectively. The former step is endothermic and the latter exothermic. The color of the sample changed to pink from bluish violet at the latter step. The latter step seems to involve the deaquation of coordinating water and the simultaneous formation of diol complex.

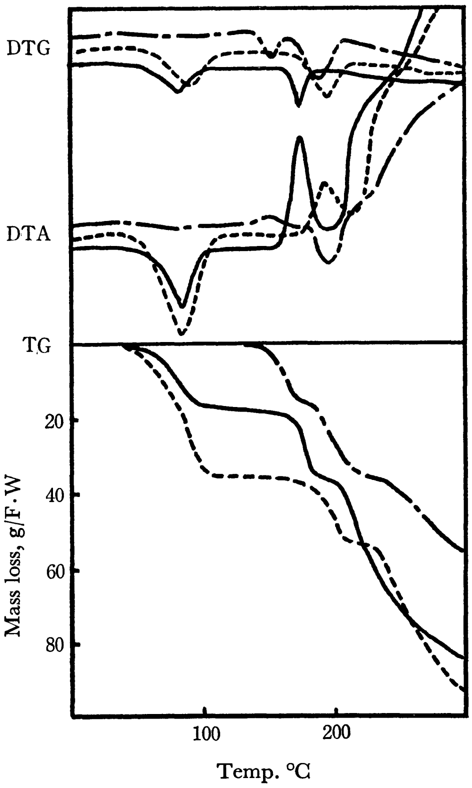

Fig. 1. Derivatograms for nta (·—·—·), nipda (······) and *l*da (——) complexes.

In complex V, the mass losses corresponding to one mole of crystalline water in an endothermic reaction and then to one mole of coordinating water in an exothermic reaction were found at 100°C and at 180°C, respectively. The color of the sample changed to pink from bluish violet at the latter step as in the case of complex II. Such a change could be observed with all complexes except for complex I.

In complex I, although the two steps of mass losses corresponding to each one mole of water were separately observed at 160°C and 180°C, the color change and the exothermic DTA peak were found only at the former step. The former step is, hence, thought to correspond to the deaquation-olation and the latter, to the liberation of crystalline water alone.

In order to compare the thermal stability of all the complexes with each other, the exothermic DTA peaks alone are sketched in Fig. 2.

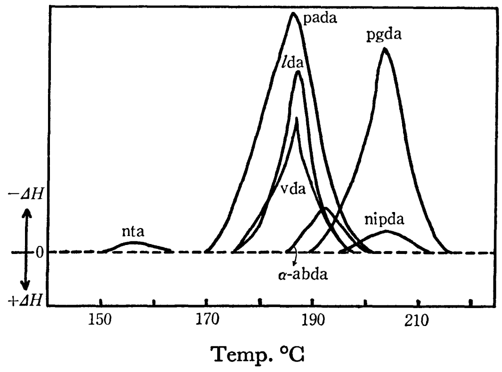

Fig. 2. DTA curves for deaquation-olation of the complexes.

The abscissa shows temperature and the ordinate an arbitrary scale of DTA curves. The dotted line gives the base of DTA curve, and $-\Delta H$ and $+\Delta H$ shows the scales for the exothermic and the endothermic reactions, respectively. As seen from the figure, although the reaction temperature differ with the kinds of the complexes, the peak area becomes larger in the order: nta- < nipda- < α-abda- < vda- < *l*da- < pgda- < pada-complexes.

Electronic Spectra. As an example, the electronic spectra of hydroxoaquo-pada-cobalt(III) complex (VII), of the complex after heating at 190°C and of diol-pada complex prepared in another method[10] are given in Fig. 3. The spectrum for complex VII after heating at 190°C, where the deaquation-olation seems to have taken place, closely resemble that of the diol complex, and the second band (due to *d-d* transition) does not appear distinctly. Similar results are also obtained in all the remaining complexes. They are in line with

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7) M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, This Bulletin, **31**, 940 (1958).

8) M. Tachibana, A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 1061 (1970).

9) A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 414 (1970).

10) To be published elsewhere.

11) R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, This Bulletin, **42**, 1881 (1969).

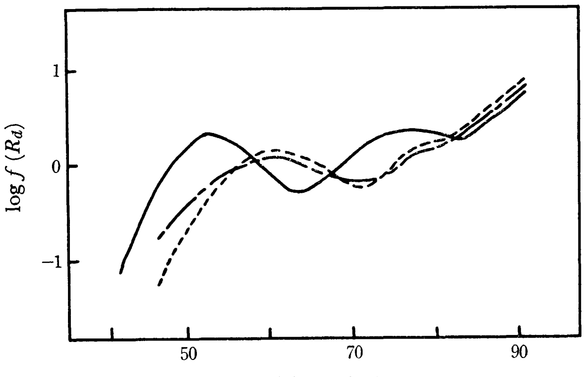

Fig. 3. Electronic spectra for K[Co(OH) pada (H_2O)]·$5H_2O$ (——), the sample after heating at 190° (–·–·–) and K_2[pada-Co$(OH)_2$Co pada] (······).

the electronic spectra for the ol-ammine-cobalt(III)[12] and the diol-nta cobalt(III) complexes.[7]

Enthalpy Change and Activation Energy. The enthalpy changes, ΔH, for each step of the thermal reactions in these complexes were estimated from DTA curves in the same way as described.[11] It was also confirmed by the analyses of DTA curves[13] that both the evolution of the crystalline water and the deaquation-olation proceed in the first order. The Arrhenius plots, log-k vs. $1/T$, for both reactions showed a good linearity. Only those for the latter reaction are given in Fig. 4. The activation energies, $E^{\neq}$, of the reactions were calculated from the slope of the respective Arrhenius plots. The values of ΔH and $E^{\neq}$ estimated in all the complexes are summarized in Table 2.

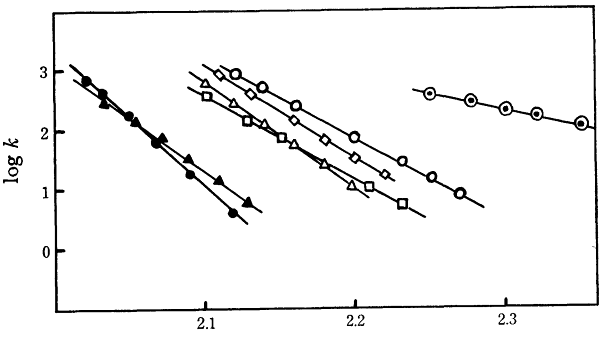

Fig. 4. Arrhenius plots for deaquation-olation of nta-(⊙-⊙), nipda-(▲-▲), α-abda-(△-△), vda-(○-○), *l*da- (□-□), pgda-(●-●), and pada-(○-○) complexes.

The values of ΔH and $E^{\neq}$ for the liberation of crystalline water from complexes II, III, IV, and V are close to the values for the reaction $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O$ ($\Delta H \approx 13.1$ kcal/mol, $E^{\neq} \approx 21.3$ kcal/mol). The five moles of crystalline water of complex VII were liberated step by step: first four moles and then one mole. The one mole was more difficult to be liberated than the four. It was found that only in the case of complex I the activation energy for the liberation of crystalline water (38.8 kcal/mol) is greater than that for the deaquation-olation (29.7 kcal/mol). It is thus considered that coordinating water can be more easily lost than crystalline water. This is in good agreement with the fact that the deaquation-olation precedes the evolution of crystalline water as shown by the lower starting temperature in the former process than that in the latter (Table 2).

In the deaquation-olation, the values of ΔH for all the complexes show an increasing trend with the structural complexities of the chelating agents. On the contrary, the inverse trend was found in the values of $E^{\neq}$ except complexes I and VI. It is not clear why complexes I and VI show a much lower and higher activation energy respectively. The numerical data in Table 2 indicate that the deaquation-olation takes place in the order: nta- < nipda- < α-abda- < vda- < *l*da- < pgda- < pada-complexes.

Proposed Thermal Reaction Mechanism. The thermal reaction mechanisms of these complexes will be discussed on the basis of the above results. Figure 5 shows the proposed thermal reaction scheme for complex I and Fig. 6 that for complexes II through VII.

It is reasonable to conclude that for complex I the crystalline water is evolved after deaquation-olation took place. On the other hand, complexes II through VII are considered first to lose the crystalline water, and then to show the deaquation-olation as in Fig. 6.

If the activated complex in the above two figures were assumed to be an intermediate in the dequation-olation, two mechanisms are possible, *viz.*, the formation of activated complex from the corresponding hydroxoaquo complex is slow or the liberation of coordinating water from the activated complex is slow. However,

Table 2. THERMOCHEMICAL FUNCTIONS FOR EVOLUTION OF CRYSTALLINE WATER AND DEAQUATION-OLATION

Complex	Evolution step of crystalline waters			Deaquation-olation step		
	Starting temp (°C)	ΔH(kcal/mol)	$E^{\neq}$(kcal/mol)	Starting temp (°C)	ΔH (kcal/mol)	$E^{\neq}$(kcal/mol)
I	175	8.2	38.8	150	−1.2	29.7
II	40	13.6	19.9	195	−4.8	85.8
III	50	13.5	21.0	185	−6.3	75.4
IV	80	13.3	21.1	175	−12.8	70.8
V	60	13.0	20.3	175	−14.3	65.1
VI				190	−18.8	91.9
VII	40 (4 mol)	12.7	16.3	170	−21.3	62.8
	90 (1 mol)	13.3	24.2			

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[12] Y. Inamura and Y. Kondo, *Nippon Kagaku Zasshi*, **74**, 627 (1953).

[13] H. J. Borchardt and F. Danniels, *J. Amer. Chem. Soc.*, **79**, 41 (1957).

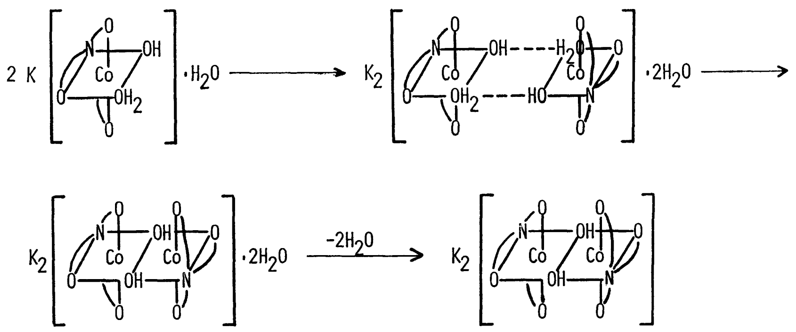

Fig. 5. Proposed thermal reaction scheme for nta-complexes.

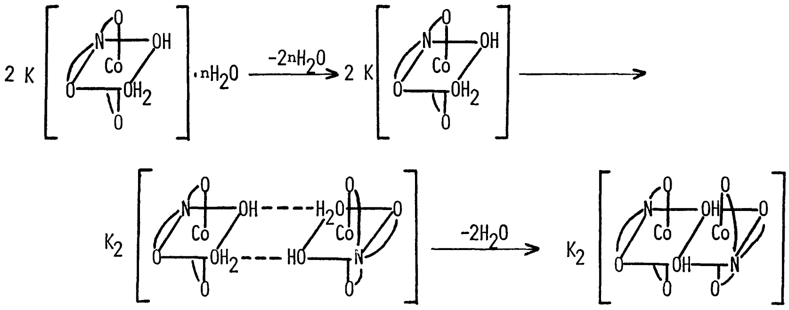

Fig. 6. Proposed thermal reaction scheme for nipda-, α-abda-, vda-, *l*da-, pgda-, and pada-complexes.

the idea that the liberation of coordinating water is slow (the rate-determining step) might be reasonable in the present deaquation-olation. It would be supported by satisfactory linearity in the Arrhenius plots which were plotted from the view point that the reaction proceeds in the first order.

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