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Derivatographic Studies on Transition Metal Complexes. I. Deaquation-Anation Reaction of Aquopentaamminechromium(III) Complexes[*1]

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By using a Derivatograph, the simultaneous analyses in TGA, DTA and DTG on the several aquopentaamminechromium(III) complexes were attempted. The enthalpy changes, ΔH, in the deaquation-anation processes of aquopentaamminechromium(III) nitrate, chloride, bromide, iodide, sulfate and sulfite were calculated as 11.9, 6.1, 9.0, 10.8, 13.8 and 12.8 kcal/mol, respectively, the activation energies, $E^{\neq}$, in the corresponding processes of the nitrate, chloride, bromide, sulfate and sulfite were obtained by the DTG curve analysis as 18, 28, 38, 36 and 33 kcal/mol, and those in the nitrate, chloride, bromide, iodide, sulfate and sulfite were obtained by the DTA curve analysis as 14, 25, 36, 19, 39 and 32 kcal/mol, respectively.

A number of thermochemical studies on the metal complexes by means of thermogravimetric analysis (TGA) with a thermobalance[1] or by means of the dissociation pressure method[2] have been reported. Since the application of the differential thermal analysis (DTA) alone to the solid phase reaction of the metal complexes in the field of thermochemical studies can not give satisfactory information on the reactions, owing to the ambiguity of the stoichiometric relation in it, simultaneous measurements of DTA, TGA and derivative thermogravimetric analysis (DTG) are indispensable for obtaining a consistent interpretation for the reactions. Nevertheless, such a technique for the simultaneous measurements of TGA and DTA was never applied until several years ago.[3]

The simultaneous measurements of TGA and DTA with a Derivatograph on the transition metal complexes with a single sample was undertaken.

[*1] Presented at the 17th Symposium on Coordination Compounds of the Chemical Society of Japan, Hiroshima, December, 1967.

1) M. Mori and R. Tsuchiya, This Bulletin, **33**, 841 (1960); N. Tanaka and M. Nanjo, *ibid.*, **37**, 1330 (1964).

2) M. Mori and R. Tsuchiya, *ibid.*, **32**, 467 (1959).

3) W. W. Wendlandt and J. L. Bear, *J. Inorg. Nucl. Chem.*, **22**, 77 (1961).

As the first series of derivatographic studies, the deaquation-anation reaction of aquopentaamminechromium(III) complexes was investigated with the above equipment and a comparison of the thermal properties between them and the corresponding cobalt(III) complexes was also made.

Experimental

Materials. The aquopentaamminechromium(III) nitrate (I) was prepared by the methods proposed by one of the authors.[4] The corresponding chloride (II), bromide (III), iodide (IV), sulfate (V) and sulfite (VI) were prepared by adding ammonium chloride and hydrochloric acid, potassium bromide and hydrobromic acid, potassium iodide, sodium sulfate and potassium hydrogen sulfite to aquopentaamminechromium(III) nitrate I as a starting material, respectively;[4] they were identified by the chemical analysis and the infrared absorption spectra.

Measurements. The TGA, DTA and DTG curves were automatic-photographically recorded with a single sample in a constant nitrogen stream with a Metrimpex Derivatograph Typ-OD-102 made in Hungary,[5] which is a most useful equipment for the simultaneous measurements of the above three curves. Five hundred milligrams of samples were used in each measurement unless otherwise stated. The particle size of the samples was within the range between 100 and 200 mesh. The heating rate was about 1°C per minute. IR and far-IR spectra of the samples, both before and after the deaquation-anation reactions, were measured with a JASCO Model IR-E IR Spectrophotometer and a Hitachi EPI Far-IR Spectrophotometer, respectively.

Results and Discussion

The derivatograms, containing T, TGA, DTA and DTG curves, recorded for the complexes, II, III and IV, are shown in Fig. 1, and those for I, V and VI are shown in Fig. 2. In these figures, TGA curves are recorded in the lower part of the chart and the other T, DTA and DTG curves are in the upper part. Recordings of DTA and DTG were operated so as to be approximately expanded within the upper part of the chart by adjusting the sensitivity of the galvanometer.

That the aquopentaamminechromium(III) complexes, $[Cr(H_2O)(NH_3)_5]X_3$ (X=halogenide, nitrate, sulfate or sulfite anion), give rise to the deaquation-anation reaction, that is, they lose the coordinated water to yield acidopentaamminechromium(III) complexes, $[CrX(NH_3)_5]X_2$, is well known.[6] The first dropping of the TGA curves and the simultaneous appearance of the endothermic peaks in DTA curves for the complexes concerned shown in Figs. 1 and 2 suggest the occurrence of such deaquation-anation processes in the solid phase.

The temperatures at which the deaquation of the aquopentaamminechromium(III) complexes begins, appearing in TGA curves, T, and the temperatures at which endothermic peaks show the maximum in DTA curves, T_m, for the respective reactions, shown in Figs. 1 and 2 are summarized in Table 1.

It is found from this table that the temperature at which the deaquation starts becomes higher in the order of $I < II < III < IV < V < VI$. This order is not in good agreement with that proposed by Wendlandt *et al.*[3] for the complexes, I, II, III and IV, but it is approximately in agreement with that reported by Tanaka *et al.*[7] for hexaamminenickel(II) complexes, so far as the nitrate, chloride, bromide and iodide are concerned. The sequence obtained in this work is approximately parallel to the increasing order of the ionic radii of the counter-anions entering into the coordination sphere after

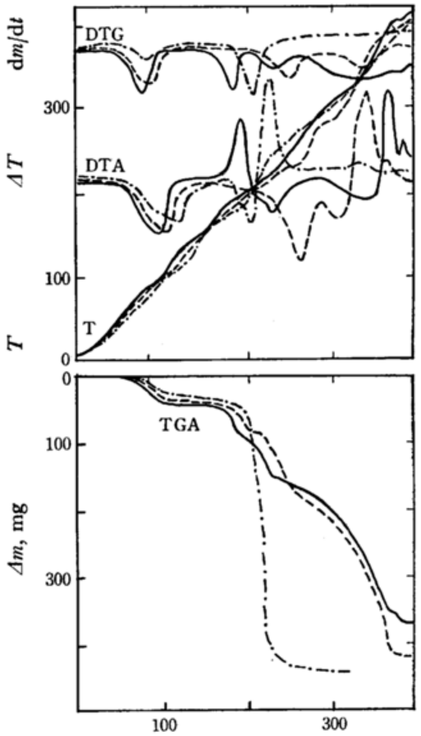

Fig. 1. Derivatograms for aquopentaamminechro mium(III) chloride (——), bromide (------) and iodide (-----).

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4) E. Kyuno, M. Kamada and N. Tanaka, This Bulletin, **40**, 1848 (1967).

5) F. Paulik, J. Paulik and L. Erdey, Hung. Patent No. 144, 548 (1954); No. 145, 469 (1955); No. 146, 461 (1956).

6) S. M. Jφrgensen, *J. Prakt. Chem.*, **18**, 209 (1878).

7) N. Tanaka, M. Kagawa and M. Kamada, Presented at the 16th Symposium on Coordination Compounds of the Chemical Society of Japan, Tokyo, December, 1966.

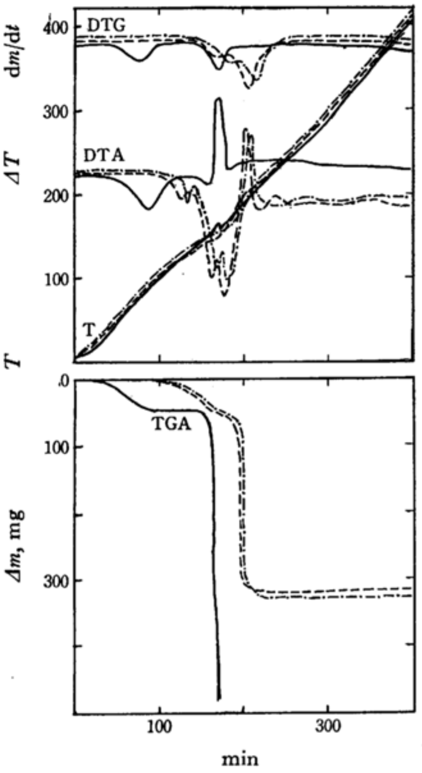

Fig. 2. Derivatograms for aquopentaamminechromium(III) nitrate (——), sulfate (------) and sulfite (-·-·-·-).

TABLE 1. THE TEMPERATURES, T, AT WHICH THE COMPLEXES BEGIN TO BE DEAQUATED AND THE PEAK TEMPERATURES, T_m (°C)

Complex	T	T_m
I	40	85
II	60	82
III	68	95
IV	70	125
V	100	134
IV	120	140

the deaquation. It may suggest the apparent increasing order of the thermal stability against the deaquation-anation reaction among the above aquopentaammine complexes concerned.

The enthalpy change, ΔH, in the deaquation-anation reaction per mole of sample is expressed as below in terms of the peak area, A, formed by DTA curves.

$$\Delta H = \frac{K}{N} A, \tag{1}$$

where K is a constant containing the conductivity of the sample and depending upon the structure of the equipment and the heating conditions, and N is the numbers of moles of sample, *i. e.*, the value of the mass divided by the molecular weight of the sample. The ratio, $\Delta H/A$, should be, therefore, the function of the dehydration temperature of the materials.

In order to confirm these relationships, the values of $\Delta H/A$ were plotted against the peak temperatures of DTA curves in the dehydration reactions in Fig. 3 for barium chloride dihydrate, cobalt(II) sulfate heptahydrate, copper(II) sulfate pentahydrate, nickel(II) sulfate heptahydrate, ammonium aluminum alum, potassium chromium(III) alum, copper(II) sulfate monohydrate and cobalt(II) sulfate pentahydrate. Since these plottings lie approximately on a smoothed curve, it may be appropriate to select copper(II) sulfate pentahydrate as a standard sample to determine the constant K in Eq. (1).

By comparing the peak area in the DTA curves in the deaquation-anation reaction of aquopentaamminechromium(III) complexes concerned with that appearing in DTA in the dehydration of copper(II) sulfate pentahydrate, and applying $\Delta H=$ 13.6 kcal/molH_2O as the mean value of the enthalpy change per one mole of water calculated from the total enthalpy change[8] in the liberation of the first four moles of water from copper(II) sulfate pentahydrate, the enthalpy change in the deaquation-anation reaction desired can be determined.

These values, ΔH, for the aquopentaamminechromium(III) complexes obtained by the above method are listed in Table 2, together with those for the aquopentaamminecobalt(III) complexes cited from reference.[9]

It is seen in this table that the values of ΔH for the complexes, I, II and III, are in remarkably good agreement with those for the corresponding

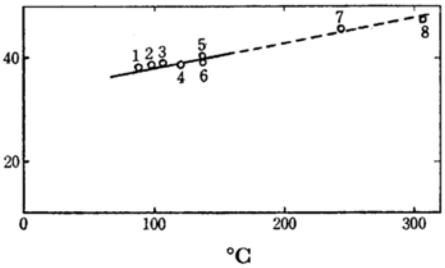

Fig. 3. Correlation of the ratio, $\Delta H/A$, *vs.* temperature.

1, $BaCl_2 \cdot 2H_2O$
2, $CoSO_4 \cdot 7H_2O$
3, $CuSO_4 \cdot 5H_2O$
4, $NiSO_4 \cdot 7H_2O$
5, NH_4-Al-Alum
6, K-Cr-Alum
7, $CuSO_4 \cdot H_2O$
8, $CoSO_4 \cdot 5H_2O$

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[8] K. Sano, *Sci. Rep. Tohoku Imp. Univ., Ser. I*, **24**, 719 (1936).

[9] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," United States Government Printing Office, Washington, D. C. (1952).

TABLE 2. ENTHALPY CHANGES, ΔH, IN THE DEAQUATION-ANATION REACTIONS OF AQUOPENTAAMMINECHROMIUM(III) AND THE CORRESPONDING COBALT(III) COMPLEXES

Complxe	ΔH kcal/mol	Complex	ΔH kcal/mol
I	11.9	$[CoH_2O(NH_3)_5](NO_3)_3$	11.6
II	6.1	$[CoH_2O(NH_3)_5]Cl_3$	6.7
III	9.0	$[CoH_2O(NH_3)_5]Br_3$	8.7
IV	10.8		
V	13.8		
VI	12.8		

cobalt(III) complexes, respectively, and the increasing order of the values, ΔH, such as in II$<$III$<$IV$<$I$<$VI$\leq$V, is approximately parallel, except for the nitrate, I, to the order of their increasing thermal stability presumed by the deaquation-anation temperatures, T or T_m, listed in Table 1.

Up to date, the kinetic analysis has, in general, been performed by the isothermal method, but it is very troublesome, though accurate, owing to the necessity of, at least, several measurements of the quantity concerning the reactants or products at various temperatures. On the contrary, the kinetic analysis in the thermal decomposition processes became very advantageous, if the DTG curve is applied, because it will be possible by using only one curve obtained by the temperature-elevating method.

The rate constant, k, is given by the equation[10]

$$k = \frac{(A/N_0)^{n-1}(-\mathrm{d}x/\mathrm{d}t)}{(A-a)^n}, \tag{2}$$

where N_0 is the number of mole of the sample at the time at which the DTG peak appears, A and a are the total peak area and the area swept up till the time, t, respectively, $\mathrm{d}x/\mathrm{d}t$ is the displacement of the DTG curve from the base line at time t, that is, parallel to the rate of the weight change, and n is the reaction order, as shown in Fig. 4.

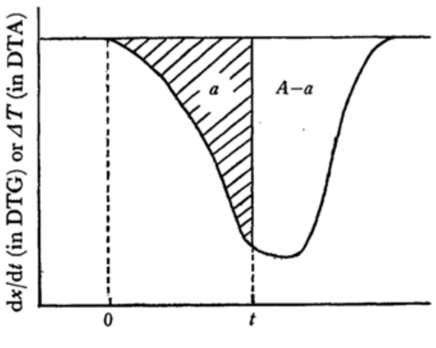

Fig. 4. Kinetic analyses on the basis of DTG and DTA curves.

If the reaction proceeds in the first order, Eq. (2) is simplified as

$$k = \frac{-\mathrm{d}x/\mathrm{d}t}{A-a}. \tag{3}$$

The logarithm values of the rate constant for the deaquation-anation reaction in the aquopentaammine complexes, I, II, III, V and VI, are calculated by using Eq. (3) and they are plotted against the reciprocal of the absolute temperature, which are shown in Fig. 5.

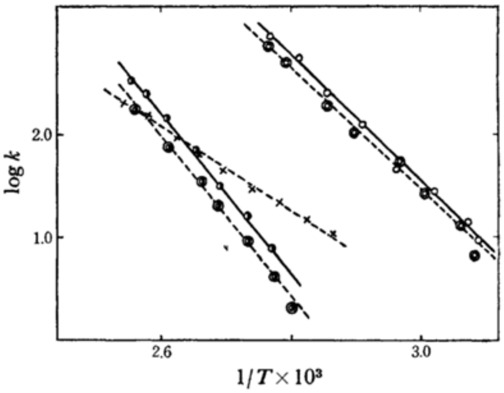

Fig. 5. Arrhenius plots, $\log k - 1/T$, for the deaquation-anation reactions of aquopentaamminechromium(III) chloride (○◎), bomide (◐◉) and iodide (×), from DTG (——) and from DTA (------).

Another available method of kinetic analysis is the use of the DTA curve. The rate constant is given by the equation[11]

$$k = \left(\frac{KAV}{N_0}\right)^{n-1} \frac{C_p(\mathrm{d}\Delta T/\mathrm{d}t) + K\Delta T}{\{K(A-a) - C_p\Delta T\}^n}, \tag{4}$$

where V is a volume of a sample, ΔT is the temperature difference between the sample and the inert material, $\mathrm{d}\Delta T/\mathrm{d}t$ expresses the slope of DTA curve at time t, and C_p is the molecular heat of the sample. ΔT is corresponding to $\mathrm{d}x/\mathrm{d}t$ in the case of DTG curve shown in Fig. 4, and other terms are identical to the corresponding ones noted in Eq. (2).

It will be difficult to find the value of the rate constant from Eq. (4), since the molecular heat is not generally known. However, when the terms containing the molecular heat in Eq. (4) are negligibly small and the reaction is assumed to proceed in the first order, Eq. (4) is simplified as

$$k = \frac{\Delta T}{A-a}. \tag{5}$$

Equation (5) can be formerly obtained by replacing $-\mathrm{d}x/\mathrm{d}t$ in Eq. (3) by ΔT, and the analytical

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[10] N. G. Dave and S. K. Chopra, *Z. Physik. Chem.*, **48**, 257 (1966).

[11] H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).

processes are quite the same in both DTG and DTA curves.

Arrhenius plots obtained for the chloride, bromide and iodide as the representatives by using Eq. (5) are also shown in Fig. 5, together with the plots by DTG analysis. The activation energies, $E^{\neq}$, obtained from the Arrhenius plots in the case of DTG and DTA analyses are summarized in Table 3.

TABLE 3. ACTIVATION ENERGIES, $E^{\neq}$, IN THE DEAQUATION-ANATION REACTIONS OF AQUOPENTAAMMINECHROMIUM(III) AND THAT OF ONE OF THE COBALT(III) COMPLEXES

Complex	$E^{\neq}$ kcal (from DTG)	$E^{\neq}$ kcal (from DTA)	$E^{\neq}$ by Wendlandt[3]
I	18	14	16
II	28	25	18
III	38	36	31
IV	—	19	18
V	36	39	—
VI	33	32	—
$[CoH_2O(NH_3)_5]Cl_3$ 22[12]			

In this table, the activation energies in the deaquation-anation reactions of aquopentaamminechromium(III) halides and nitrate reported by Wendlandt *et al.*[8] and that of the corresponding aquopentaamminecobalt(III) chloride reported by one of the authors[12] are also included, which was, however, obtained by the isothermal kinetic measurement different from those in the present work by the dynamic temperature-elevating method.

That nitrate has the smallest value of activation energy supports the fact that nitrate has the lowest dissociation temperature of all the complexes treated in this paper and undergoes deaquation most easily.

Although the methods to obtain the activation energy employed by authors in this study and by Wendlandt *et al.*, so far as the nitrate and the halides are concerned, are different from each other, the data by two groups of workers are in satisfactory agreement with one another except for those of the chloride.

If these deaquation-anation reactions belong to S_N1 reaction, *i. e.*, the rate-determining step in these reactions consists in the deaquation process such as

$$N_5Cr\text{-}OH_2 \longrightarrow N_5Cr + OH_2\,, \qquad \text{(a)}$$

where N_5Cr expresses $Cr(NH_3)_5$ group, the activation energies in these reactions should be approximately close to each other. But it is not always the case as shown in Table 3. When the rate of the anation process such as,

$$N_5Cr + X \longrightarrow N_5CrX\,, \qquad \text{(b)}$$

where X expresses halide ions, nitrate, sulfate or sulfite anions, is larger than that of the deaquation process, (a), the deaquation-anation reaction will belong to S_N1 reaction owing to the rate-determining step of (a) as described above, whereas the rate of the process (b) is smaller than that of the process (a), the reaction will belong to S_N2 reaction due to the rate-determining step of (b).

The fact given in Table 3 that the activation energies in the deaquation-anation reactions of the bromide, sulfate and sulfite are, above all, larger than those of the chloride, iodide and nitrate, suggests that the deaquation-anation reactions in the former complexes, the bromide, sulfate and sulfite, include, to some extent, the tendency of S_N2 reaction, at least, at the earlier step of these reactions, differing from those in the latter complexes. The reason for this may be attributed to the larger ionic radii of the bromide, sulfate and sulfite anions, but a more decisive reason is not clear.

That the activation energy for the aquopentaamminechromium(III) chloride is slightly larger than that for the corresponding cobalt(III) chloride as shown in the table may be due to a somewhat larger force constant in $Cr\text{-}OH_2$ in the former complex than that in $Co\text{-}OH_2$ in the latter one.[13]

The authors wish to express their appreciation to the Ministry of Education for the financial support granted for this research.

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12) M. Mori, R. Tsuchiya and Y. Okano, This Bulletin, **32**, 1029 (1959).

13) T. Shimanouchi, I. Nakagawa and J. Shiraishi, Presented at the 12th Symposium on Coordination Compounds of the Chemical Society of Japan, Tokyo, December, 1962.