Thermochimica Acta, 20 (1977) 417–421

THE KINETICS OF OLATION OF SOME HYDROXOAQUOTETRAMMINE-COBALT(III) COMPLEXES IN THE SOLID STATE

P. R. NAMBIAR AND W. W. WENDLANDT*
Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)
(Received 20 October 1976)

ABSTRACT

The solid-state kinetics for the olation reactions of $[Co(NH_3)_4(OH)(H_2O)]X_2$ (where X = Cl^-, Br^-, or $\frac{1}{2}SO_4^{2-}$) were determined by several different methods using dynamic and isothermal thermogravimetric data. For the reduced-time plot method, *E* values were 20, 43, and 25 kcal mol^{-1} for the chloride, bromide, and sulfate complexes, respectively. For the Jacobs and Kureishy method, *E* values of 21, 37, and 17 kcal mol^{-1}, were obtained for the above three complexes, respectively. A possible reaction pathway is suggested for the olation reaction.

INTRODUCTION

The solid-state olation reaction exhibited by hydroxoaquotetramminecobalt (III) complexes[1] is a combination of two chemical processes: (1) the elimination of a water molecule; and (2) the formation of two hydroxo bridges between two molecules. The former process is endothermic while the latter is exothermic. It is evident from the DTA curves of hydroxoaquotetramminecobalt(III) complexes[1] that the energy for the bridge formation is less than that for the deaquation reaction. Energywise, the exothermic effect of the bridge formation is less than that of the deaquation reaction since both processes take place almost simultaneously. It seems, therefore, that the results of previous DTA studies on the kinetics of the olation reaction do not represent any of the two processes mentioned but only the net reaction. This reaction is, in a way, analogous to the deaquation and anation of $[Co(NH_3)_5(H_2O)]X_3$ complexes[2] except for bridge formation instead of anation. Since the activation energy for this process has been attributed[2] to the first step, i.e., deaquation, and since it is reasonable to presume that deaquation would be the rate-determining step in olation also, it was thought worthwhile to study the kinetics of olation reactions by the thermal analysis technique of thermogravimetry. Also, this study could serve as a check on the activation energy values of these compounds since

---

* To whom communications should be addressed.

similar compounds with amino acid ligands in the place of ammonia have been reported[3] to undergo olation with the relatively high values of 70.7–97.2 kcal mol^{-1} for the activation energies.

EXPERIMENTAL PART

Preparation of compounds

The compounds, $[Co(NH_3)_4(OH)(OH_2)]Cl_2$, $[Co(NH_3)_4(OH)(OH_2)]Br_2$, and $[Co(NH_3)_4(OH)(OH_2)]SO_4$ were prepared and characterized according to methods described in the literature[4, 5]. Water contents of the complexes were determined by mass-loss on the thermobalance.

Apparatus

Dynamic thermogravimetry data were obtained using a DuPont Model 950 Thermogravimetric Analyzer at a heating rate of 8°C min^{-1}. Isothermal data were obtained on a Cahn RG Electro-balance converted to a thermobalance. A dynamic nitrogen atmosphere was used in all of the studies.

RESULTS AND DISCUSSION

The isothermal thermogravimetry data were analyzed using reduced time plots. This method, which is due to Sharp et al.[6], aids in the rapid selection of appropriate rate equations describing the kinetics. In the case of each of the compounds studied, the master plot for the theoretical expressions was superimposed over the reduced time plots obtained experimentally. These experimental plots are shown in Fig. 1. For $[Co(NH_3)_4(OH)(OH_2)]Cl_2$ and $[Co(NH_3)_4(OH)(OH_2)]Br_2$, it was observed that the first order decay law fits the experimental data most closely. The law, in general, should be valid to the very end of the reaction but in these cases the fit is only up to $\alpha = 0.5$. This law, which is derived on the basis of nucleation of particles by

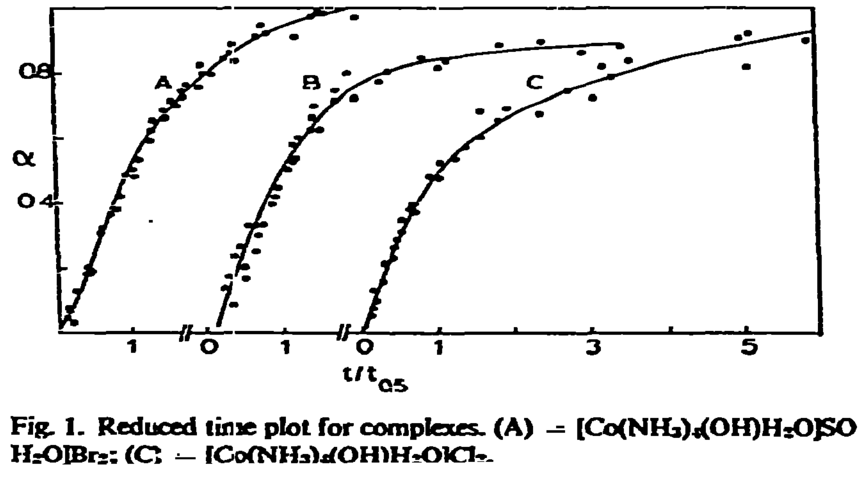


Fig. 1. Reduced time plot for complexes. (A) = $[Co(NH_3)_4(OH)H_2O]SO_4$; (B) = $[Co(NH_3)_4(OH)H_2O]Br_2$; (C) = $[Co(NH_3)_4(OH)H_2O]Cl_2$.

an exponential law followed by rapid two-dimensional growth[7], suggests that random nucleation occurs in the olation reaction of these compounds. In the case of $[Co(NH_3)_4(OH)(OH_2)]SO_4$, both the first order decay law and the contracting sphere model fit the experimental data but the former gives a better fit.

Based on these observations the rate constants were determined using the first order decay equation. The Arrhenius plots for the olation reaction of the three compounds are shown in Fig. 2 while the kinetic results are summarized in Table 1.

The thermogravimetric data were also analyzed using the general method introduced by Jacobs and Kureishy[8]. The log $(t_{(n+1)} - t_n)$ vs. $1/T$ plots obtained for the compounds studied in this investigation are shown in Fig. 3. The values of the activation energy obtained by this method are close to those obtained using the first order decay equation and are given in Table 2.

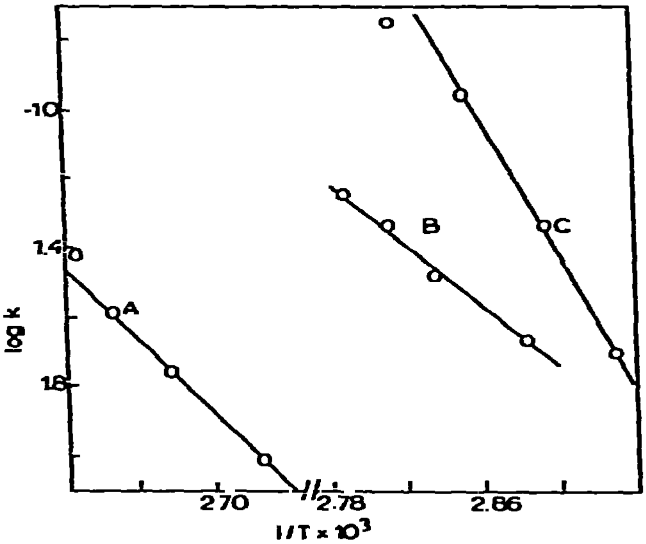


Fig. 2. Arrhenius plots for complexes. (A) = $[Co(NH_3)_4(OH)H_2O]SO_4$; (B) = $[Co(NH_3)_4(OH)H_2O]Cl_2$; (C) = $[Co(NH_3)_4(OH)H_2O]Br_2$.

TABLE 1

KINETIC DATA FOR OLATION REACTION

Complex	$[Co(NH_3)_4(OH)(OH_2)]Cl_2$		$[Co(NH_3)_4(OH)(OH_2)]Br_2$		$[Co(NH_3)_4(OH)(OH_2)]SO_4$	
	Temp. (°C)	$k \times 10^3$	Temp. (°C)	$k \times 10^3$	Temp. (°C)	$k \times 10^3$
	74	21.4	68	19.5	94	6.9
	80	32.7	73	45.7	100.5	17.6
	83	45.5	78	110.4	105	25.5
	86	56.2	83	177.2	107.7	38.8
E(kcal mol^{-1})	20		43		25	
A(min^{-1})	8.8×10^{11}		4.6×10^{16}		4.4×10^{13}	

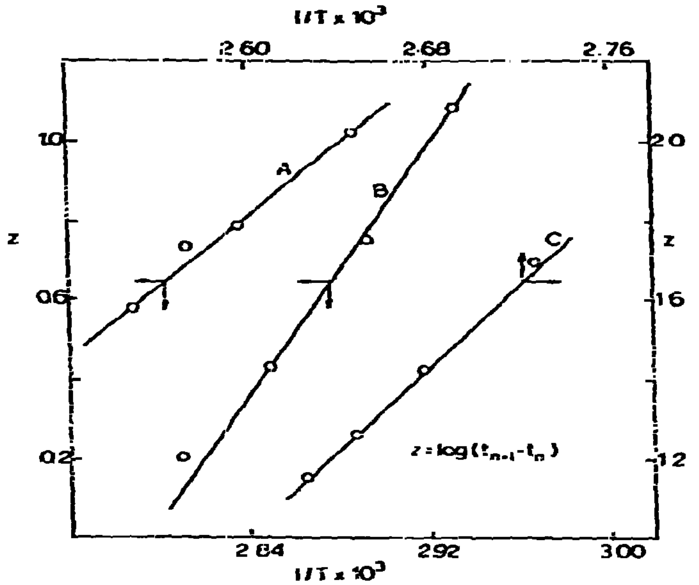


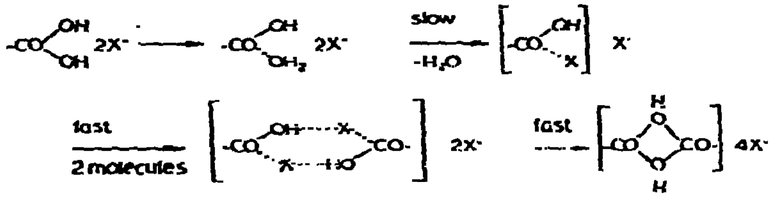
Fig. 3. Log $(t_{n-1} - t_n)$ plots for complexes. (A) — $[Co(NH_3)_4(OH)H_2O]Cl_2$; (B) — $[Co(NH_3)_4(OH)H_2O]Br_2$; (C) — $[Co(NH_3)_4(OH)H_2O]SO_4$.

TABLE 2

KINETIC RESULTS BY JACOBS AND KURESHY[8] METHOD

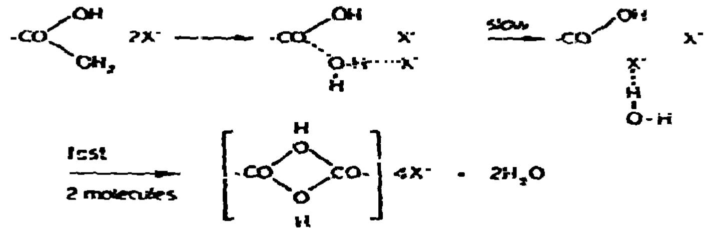
Compound	*E* *(kcal mol⁻¹)*	*a*
$[CO(NH_3)_4(OH)(H_2O)]Cl_2$	21	0.1–0.5
$[CO(NH_3)_4(OH)(H_2O)]Br_2$	37	0.1–0.5
$[CO(NH_3)_4(OH)(H_2O)]SO_4$	17	0.1–0.5
	24	0.5–0.85

A comparison of the activation energy values obtained in this investigation with those obtained previously from a DTA study[1] shows that the former values are somewhat higher. A possible explanation for this difference lies perhaps in the techniques employed for the kinetic studies. Also, the mechanism of the olation reaction in the solid state decides, to a large extent, the magnitude of the activation energy. The rate-determining step could be either the bond breaking associated with the deaquation or the bond formation reaction. The activation energy increases in the order: chloride < sulfate < bromide; this indicates that the rate-determining step is being influenced by the anion. One possibility for the reaction mechanism is as follows:



This would necessitate the formation of a hydroxoanion compound as an intermediate which may not be stable at the temperature studied. The activation energy for the bromide may be higher because of the larger size of the Br^- ion and also because it is not so strong a ligand, and does not replace the water ligand as readily as Cl^-. This type of mechanism accounts for the high *E* values reported for compounds with bulky ligands but fails to explain why the bromide should have a higher value of *E* than the sulfate.

A second possible mechanism is for hydrogen-bond formation to play a role in the deaquation process. This may be depicted by the reaction:



This reaction seems to explain the observed changes of *E*. Precise knowledge of the nature of the mechanism of olation must, however, await further experimental evidence.

ACKNOWLEDGMENT

This work was supported by the Robert A. Welch Foundation of Houston, Texas.

REFERENCES

1 W. W. Wendlandt and J. K. Fisher, *J. Inorg. Nucl. Chem.*, 24 (1962) 1685.
2 R. H. Gore and W. W. Wendlandt, *Thermochim. Acta*, 1 (1970) 491.
3 R. Tsuchiya, A. Uehara and E. Kyuno, *Bull. Chem. Soc. Japan*, 46 (1973) 3737.
4 A. Werner, *Ber.*, 40 (1907) 4434.
5 S. M. Jorgensen, *Z. Anorg. Allg. Chem.*, 2 (1892) 279.
6 J. H. Sharp, G. W. Brindley and B. N. N. Achar, *J. Am. Ceram. Soc.*, 49 (1966) 379.
7 R. S. Bradley, J. Colvin and J. Hume, *Proc. Roy. Soc.*, *A*, 137 (1932) 531.
8 P. W. M. Jacobs and A. R. T. Kureishy, *J. Chem. Soc.*, 910 (1964) 4718.