*Inorganica Chimica Acta*, 35 (1979) L329–L330
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

# Base-catalyzed Solvolysis of Some Alkylaminepentaamminecobalt(III) Complexes in Ethylenediamine

S. BALT, M. W. G. de BOLSTER and H. J. GAMELKOORN

*Department of Inorganic Chemistry, Free University, De Lairessestraat 174, 1075 HM Amsterdam, The Netherlands*

Received March 23, 1979

In our laboratory during the past years we have been successful in establishing the mechanism of the base-catalyzed ammoniation of cobalt(III) amine complexes to be strictly analogous to the conjugate-base mechanism for base-hydrolysis in aqueous solution [1–3]. As a continuation of these studies it seemed of interest to explore the solvolysis reactions of the cobalt complexes in alkyl-substituted amines. As steric effects are powerful mechanistic criteria for the dissociative activation of the conjugate-base mechanism [4–6] the project was started with a series of compounds of increasing steric crowding. To this end the solvolysis of $Co(NH_3)_5(NH_2R)^{3+}$ (R = H, $CH_3$, $C_2H_5$, n- and iso-$C_3H_7$) in ethylenediamine was chosen because this system proved to be characterized by simple kinetics with a single rate-determining step and convenient rates at ambient temperature.

## Experimental

### *Chemicals*

Preparation of the alkylaminepentaamminecobalt (III) nitrates has been described elsewhere [7]. Ethylenediammonium diperchlorate was prepared by treating a mixture of ethylenediamine and isopropanol (1:3 V/V) under cooling dropwise with concentrated perchloric acid. The precipitate formed was filtered off and recrystallized from anhydrous ethanol. Ethylenediamine was purified and dried by distillation from calcium hydride.

### *Kinetics*

In order to observe strictly anhydrous conditions all kinetic runs were performed in a closed system under an atmosphere of dried (KOH) nitrogen.

The extent of the reactions was monitored at 460 nm with an Optica CF4 DR Spectrophotometer using a specially constructed cell of 3.5 cm optical pathlength. The procedure of filling the cell and starting the reaction has been described earlier (cell 2 of reference [1]). The ionic strength was fixed at 0.15 mol $kg^{-1}$ by adding the calculated amount of dried potassium perchlorate. The complex concentrations were (3–5) × $10^{-3}$ mol $kg^{-1}$.

By way of circulating thermostatted water through the cell-walls the temperature inside the cell could be kept constant within 0.2 °C. In all cases the end product of the reaction was the tris(ethylenediamine)-cobalt(III) complex. It may safely be assumed that under the reaction conditions the complexes will be completely ion-associated as the perchlorates and the acid added as the ethylenediammonium diperchlorate will be present as $(en + H)\cdot ClO_4$.

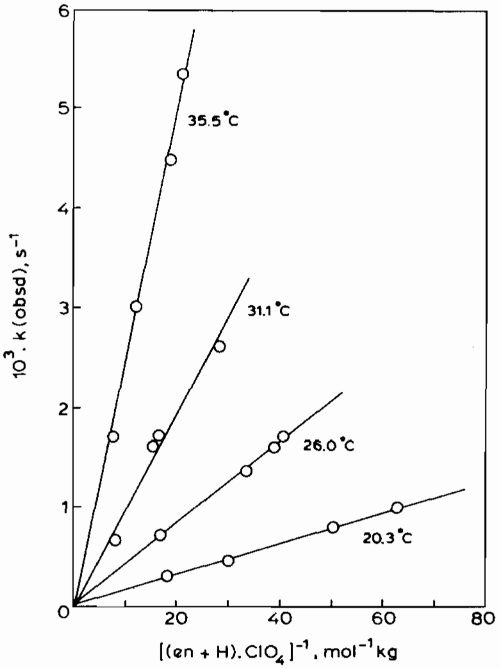

Fig. 1. Observed rate constant for the solvolysis of $[Co(NH_3)_5(NH_2C_2H_5)](ClO_4)_3$ in anhydrous ethylenediamine as a function of the concentration of added acid.

## Results and Discussion

The measured absorbance as a function of time in all cases obeyed a first-order rate law (fit better than 1%). The resulting rate constant $k_{obsd}$ as a function of the concentration of added acid – denoted as $[(en + H)\cdot ClO_4]$ – is given by:

$$k_{obsd} = k[(en + H)\cdot ClO_4]^{-1} \qquad (1)$$

as shown by representative plots for the ethylamine compound at various temperatures in Fig. 1. Values of k were obtained by least-squares fitting and are collected in the Table. In all cases the acid-independent part is zero within the experimental error. Eyring plots showed no curvature; results of a weighted least-squares analysis are also presented in the Table. The results obtained can be explained by the conjugate-base mechanism applied to amine solvents [1, 3], consisting of a rapid deprotonation (of

TABLE I. Rate and Activation Parameters for the Solvolysis of $[Co(NH_3)_5(NH_2R)](ClO_4)_3$ in Ethylenediamine.

| R | T (°C) | $10^6$ k ($s^{-1}$ mol $kg^{-1}$) | $\Delta H^{\ddagger}$ (kJ $mol^{-1}$) | $\Delta S^{\ddagger}$ (J $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|
| H | 23.1 | 0.41 | 141 ± 5 | 108 ± 15 |
| | 29.3 | 1.37 | (202)[a] | (51)[a] |
| | 35.1 | 3.55 | | |
| | 41.0 | 11.7 | | |
| $CH_3$ | 20.3 | 9.15 | 135 ± 5 | 118 ± 16 |
| | 27.0 | 36.0 | | |
| | 33.6 | 100 | | |
| | 37.6 | 222 | | |
| $C_2H_5$ | 20.3 | 15.4 | 136 ± 5 | 124 ± 15 |
| | 26.0 | 40.8 | | |
| | 31.1 | 107 | | |
| | 35.5 | 253 | | |
| n-$C_3H_7$ | 20.2 | 19.0 | 139 ± 5 | 139 ± 16 |
| | 25.2 | 52.2 | | |
| | 30.2 | 119 | | |
| | 35.0 | 322 | | |
| iso-$C_3H_7$ | 17.4 | 117 | 136 ± 5 | 148 ± 16 |
| | 20.1 | 210 | | |
| | 24.3 | 425 | | |
| | 28.0 | 912 | | |

[a] Corresponding values for base-hydrolysis from reference [8].

either $NH_3$ or $NH_2R$) pre-equilibrium (governed by the equilibrium constant $K^{CB}$) to form the conjugate base of the complex, followed by the dissociative rate-determining elimination (rate constant $k_1$) of one of the coordinated amines ($NH_3$ or $NH_2R$). In this scheme it is irrelevant (and not open to observation) which group is deprotonated and which one is the first to leave. In a series of rapid consecutive reactions three ethylenediamine molecules will then be coordinated. These steps are expected to show a progressive increase in rate as coordinated ethylenediamine labilizes the other ligands [2].

The observed pseudo first-order rate constant $k_{obsd}$ is then given by [1]:

$$k_{obsd} = k_1K^{CB}[(en + H)\cdot ClO_4]^{-1} \qquad (2)$$

Combination with the empirical equation (1) gives $k = k_1K^{CB}$.

The reactions are too fast in the accessible temperature range to separate $k_1$ and $K^{CB}$ by studying the reactions under acid-free conditions as was done for liquid ammonia [1].

A comparison of the activation parameters for the hexaammine in aqueous solution [8] (formulating the base-hydrolysis reaction analogous with the present case) and in ethylenediamine (see the Table) brings out the large enhancement of the solvolysis rate on going to the amine solvents, as noted earlier for liquid ammonia [1, 2]. This conclusion is reinforced by the absence of a spontaneous solvolysis term, even in acidic ethylenediamine solutions. Besides the form of the rate law, the observed steric effects are also indicative of the dissociative activation of a conjugate-base mechanism. For the base-hydrolysis of complexes $Co(NH_2R)_5Cl^{2+}$ in aqueous solution it has been concluded that electronic and solvation effects are unimportant in determining the relative rates in the series of complexes [4, 5]. Extension of this conclusion to the present study means that only steric effects are responsible for the rate pattern. The Table shows an increase of the rate on increasing steric crowding, with large "jumps" on going from $NH_3$ to $NH_2CH_3$ and from n- to iso-$NH_2C_3H_7$, as expected from the results of the reactions mentioned above and model calculations [4]. The explanation of the steric effects will then be steric crowding in the ground state, which is partially relieved in the transition state by dissociative bond-stretching.

It is noteworthy that the activation parameters in the Table show the rate increase on increasing the volume of the alkyl group to be mainly located in the entropy of activation, while the enthalpy of activation remains constant within the experimental error. Unfortunately no theory is available as yet to specify this effect in terms of mechanism.

The final conclusion of this study is that the conjugate-base mechanism is operative in the systems studied. We intend to extend the project to other cobalt(III) amine complexes and other amine–solvent systems to include a more detailed comparative study of stereochemistry and solvation effects.

## Achnowledgements

The authors are grateful to Mrs. G. J. Verbaan-Buter and Dr. W. B. Roolvink for their help in setting up the experiment.

## References

1 S. Balt and G. F. Pothoff, *J. Coord. Chem.*, *4*, 167 (1975).
2 S. Balt and W. de Kieviet, *J. Inorg. Nucl. Chem.*, in press.
3 S. Balt, *Inorg. Chem.*, *18*, 333 (1979).
4 D. A. Buckingham, B. M. Foxman and A. M. Sargeson, *Inorg. Chem.*, *9*, 1790 (1970).
5 Th. W. Swaddle, *Can. J. Chem.*, *55*, 3166 (1977).
6 R. A. Henderson and M. L. Tobe, *Inorg. Chem.*, *16*, 2576 (1977).
7 M. W. G. de Bolster and J. W. M. Wegener, *J. Inorg. Nucl. Chem.*, *39*, 1459 (1977).
8 S. Balt, J. Breman and C. Dekker, *J. Inorg. Nucl. Chem.*, *38*, 2023 (1976).