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# Deuterium Isotope Effect on the Kinetics of Aquation of Dichloro(β,β′,β″-Triaminotriethylamine)Cobalt(III) Ion

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*The kinetics of acid hydrolysis of* $Co(tren)Cl_2^+$ *(tren = β,β′,β″-triaminotriethylamine) and* $Co(tren\text{-}d_6)_2^+$ *have been studied in* $H_2O$ *and* $D_2O$ *at 25°. The solvent and β-deuterium isotope effects for these complexes are quite different from those observed for other* $Co^{III}$*-amine complexes. These data indicate that the solvent isotope effect is dependent on the nature of the complex, and provide further support for the proposed distortion of tren complexes.*

## Introduction

A considerable amount of kinetic data has been reported for the first aquation step of dihalo-octahedral cobalt(III)-amine complexes. In all complexes of this type which have been studied, acid hydrolysis occurs in two steps, the first of which is replacement of one halide with $H_2O$,

$$CoN_4X_2^+ + H_2O \xrightarrow{k_1} CoN_4(H_2O)X^{2+} + X^-$$

where N represents a nitrogen from a mono or polyamine and X represents a halide ion.

Recently, the kinetics of the first aquation step of $Co(tren)Cl_2^+$ (tren = β,β′,β″-triaminotriethylamine) have been investigated.[1] This study showed the first aquation step of $Co(tren)Cl_2^+$ to proceed at a rate 1200 times faster than the rate for *cis***-$Co(en)_2Cl_2^+$ under similar conditions. The faster rate of reaction of $Co(tren)Cl_2^+$ has been attributed to a distortion of this complex by the tren ligand.

Basolo and others[2] have suggested the possibility that a solvent-assisted pathway involving hydrogen-bonding of the solvent $H_2O$ to the amine hydrogens and to the leaving group is important in the mechanism of these aquation reactions.

The kinetic deuterium isotope effect has been found useful for the investigation of solvent assistance in these aquation reactions because either the solvent, water, or the β-amine hydrogens of the ligand can be deuterated. The aquation of $Co^{III}$-tren complexes seems especially interesting because distortion in these complexes might affect any proposed hydrogen bonding or solvent assistance, which could be determined by comparing the kinetic isotope effects for these complexes with those for regular octahedral systems, *i.e.*, $Co(en)_2Cl_2^+$. Therefore, the present study was initiated.

## Experimental Section

*Preparation of Compounds. Dichloro(triaminotriethylamine)cobalt(III) chloride Hemihydrate and Dichloro(triaminotriethylamine)cobalt(III) perchlorate* were made by a previous method.[3] *Dichloro(triaminotriethylamine-*$d_6$*)* cobalt(III) perchlorate was prepared by a method similar to that reported for *cis*–$[Co(trien\text{-}d_6)Cl_2]ClH_2O$.[4] The purity of the deuterated complex was indicated by the complete disappearance of N–H bonds in the infrared spectrum. $D_2O$ (99.77%) was obtained from Columbia Chem. Co.

*Kinetic Measurements*

All kinetic measurements were made spectrophotometrically using a Cary Model 14 Spectrophotometer with matched cells of 1 cm path length. The temperature was controlled to within ±0.1° by circulating thermostatted water through the cell compartment. The concentration of complex used was 3mM. The reaction was followed at 529 nm, where the maximum difference between the reactant and product (chloroaquo) species occurs. Some measurements were also carried out at 508 nm (the isosbestic wavelength of the second aquation step) with nearly identical results.

The pseudo-first-order rate constants were obtained from the slope of a least squares plot of log $(A_\infty - A_t)$ *vs.* t where $A_\infty$ is the final absorbance reading and $A_t$ is absorbance at time t. The plots all gave straight lines for at least 92% of the reaction.

To confirm the fact that exchange of hydrogen between solvent and complex was not occurring before or during aquation, and thus invalidating the kinetic measurements, a solution at the appropriate temperature, ionic strength, and complex concentration was left for an hour, after which the solvent was distilled off under vacuum. Infrared examination of the pur-

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(**) en = ethylenediamine.

[1] S.K. Madan, W.M. Reiff, and J.C. Bailar, Jr., *Inorg. Chem.*, *4*, 1366 (1965).

[2] F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions », 2nd ed., John Wiley and Sons, pp. 134-135.

[3] W.V. Miller and S.K. Madan, *Inorg. Chem.*, *10*, 1250 (1971).

[4] D.A. Buckingham and D. Jones, *Inorg. Chem.*, *4*, 1387 (1965).

ple chloroaquo product obtained showed unchanged N–H stretching bands and no evidence of any N–D vibrations.

## Results and Discussion

Madan and Reiff[1] measured the $k_1$ values for the first aquation of $Co(tren)Cl_2^+$ and found that the reaction was pseudo-first-order, and that variation in the initial concentration of the complex did not affect the rate constant $k_1$.

Table I summarizes the rate constants measured for the first aquation step of $Co(tren)Cl_2^+$ and $Co(tren{-}d_6)Cl_2^+$ in both $H_2O$ and $D_2O$ at pH 1. It can be seen that deuteration of the solvent, of the beta-hydrogens of the complex, or of both results in a lowering of the rate constant $k_1$, with the biggest decrease found when both are deuterated. This decrease in aquation rate with deuterium substitution has been found with several other cobalt(III)-amine complexes.[5-7]

**Table I.** Rates of Aquation of $Co(tren)Cl_2^+$ and $Co(tren{-}d_6)Cl_2^+$ at 25° and pH 1 in 0.12 *M* *p*-toluenesulfonic acid

| Complex | Solvent | $10^3 k_1 sec^{-1}$ |
|---|---|---|
| $Co(tren)Cl_2^+$ | $H_2O$ | 2.99±0.04 |
| $Co(tren)Cl_2^+$ | $H_2O$* | 2.98±0.03 |
| $Co(tren)Cl_2^+$ | $D_2O$ | 2.38±0.01 |
| $Co(tren{-}d_6)Cl_2^+$ | $H_2O$ | 2.11±0.04 |
| $Co(tren{-}d_6)Cl_2^+$ | $D_2O$ | 1.70±0.05 |

* Carried out in 0.1 *M* $HClO_4$.

From the data in Table II and III it can be observed that for all complexes, with the exception of the $Co^{III}$-tren species, the rate constant ratios for the solvent and for the beta-deuterium isotope effect are almost identical. This is particularly surprising because the measurements were made by two different investigators and by two different methods, spectrophotometry and titrimitry. These similar ratios are found for the regular octahedral complexes, while complexes of tren, distorted due to strain in the tren ligand, show very different ratios.

Because of the nearly constant solvent effect ratio for the $Co^{III}$-amine complexes studied previously, it has been suggested that this solvent effect is determined only by the difference in solvating ability of $H_2O$ and $D_2O$. The $k_{H_2O}/_{D_2O}$ ratio for the normal tren complex has been found in this study to be 10% lower than the average value for the regular octahedral complexes. This tends to suggest that if the complex itself is sufficiently different, it also can have an effect on this ratio.

The solvent effect ratio $k_{H_2O}/_{D_2O}$ is seen from Table II to be the same for the tren and deuterated tren species, but different for the other complexes. Similarly, the beta isotope effect for the tren complex is the same in $H_2O$ or $D_2O$, but quite different in these two solvents for the other complexes. Clearly, these results suggest that the existence of a state in which a specific interacion occurs beween the solvent molecules and the beta hydrogens (and possibly the leaving group as mentioned by Basolo[2]) would seem to be less important in the distorted tren complexes than in regular octahedral complexes.

**Table II.** Solvent Isotope Effect for $Co^{III}$-amine Complexes.

| Complex | $k_{H_2O}/k_{D_2O}$ | Complex | $k_{H_2O}/k_{D_2O}$ | Ref. |
|---|---|---|---|---|
| $Co(tren)Cl_2^+$ | 1.26 | $Co(tren{-}d_6)Cl_2^+$ | 1.26 | this work |
| *cis*-$Co(en)_2Cl_2^+$ | 1.40 | cis-$Co(en{-}d_4)_2Cl_2^+$ | 1.24 | 6 |
| *trans*-$Co(en)_2Cl_2^+$ | 1.40 | trans-$Co(en{-}d_4)_2Cl_2^+$ | 1.23 | 6 |
| $Co(NH_3)_5Cl_2^+$ | 1.41 | $Co(ND_3)_5Cl_2^+$ | 1.22 | 5 |
| $Co(en)_2(am)Cl_2^+$ * | 1.38-1.44 | | | 7 |

* am = primary amine.

**Table III.** Beta-deuterium Isotope Effect for $Co^{III}$-amine Complexes.

| Complex | Solvent | $k_h/k_d$ | Solvent | $k_h/k_d$ | Ref. |
|---|---|---|---|---|---|
| $Co(tren)Cl_2^+$ | $H_2O$ | 1.42 | $D_2O$ | 1.40 | this work |
| *cis*-$Co(en)_2Cl_2^+$ | $H_2O$ | 1.32 | $D_2O$ | 1.15 | 6 |
| *trans*-$Co(en)_2Cl_2^+$ | $H_2O$ | 1.31 | $D_2O$ | 1.15 | 6 |
| $Co(NH_3)_5Cl_2^+$ | $H_2O$ | 1.31 | $D_2O$ | 1.16 | 5 |

From the rate constants in Table I, the ratios needed to evaluate both the solvent isotope effect ($k_{H_2O}/k_{D_2O}$) and the beta-deuterium isotope effect ($k_h/k_d$) can be calculated. Tables II and III compare these ratios with the corresponding ratios for some regular octahedral cobalt amines.

Further study of the deuterium isotope effect in the reactions of octahedral coordination compounds is needed to better understand this phenomena.

(5) R.G. Pearson, N. Stellwagen, and F. Basolo, *J. Am. Chem. Soc.*, *82*, 1077 (1960).
(6) S.C. Chan, *J. Chem. Soc.*, 418 (1965).
(7) S.C. Chan and F. Leh, *ibid.* (*A*), 2010 (1967).