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Substitution Reactions of Metallic Complexes of 2,2′,2″-Triaminotriethylamine. XV. Kinetics of the Primary Acid Hydrolysis of the Dichloro(2,2′,2″-triaminotriethylamine)cobalt(III) Cation in Water–Alcohol Mixtures

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Abstract

The kinetics of the primary acid hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$ have been measured in methanol– and ethanol–water mixtures of alcohol mole fractions 0.05, 0.10, 0.15 and 0.20. In all the solvents investigated the primary acid hydrolysis occurs via a dissociative mechanism. The rate constants and thermodynamic activation parameters were determined. The dependence of the rate constant of the mole fraction, dielectric constant and ionizing power of the solvent was investigated.

Introduction

In the past, there has been much interest in the properties of mixed solvents and their effects on chemical behavior [1–4]. The investigation of inorganic reactions in mixed solvents has progressed at a notably slower rate than that of organic reactions. One reason for this is the poor solubility of inorganic complexes in mixed solvents. As a result, the majority of kinetic studies of inorganic complexes in mixed solvents have been the solvolysis reactions of inorganic complexes in aqueous–alcohol solvents [5–18]. In most studies of solvolysis reactions involving Co(III) complexes, the kinetics are complicated by *cis–trans* isomerization. Due to its stereochemical configuration, the tripodal 2,2′,2″-triaminotriethylamine (tren) ligand has been found to form complexes of the *cis* configuration only. This effectively prevents the complicating *cis–trans* isomerization reactions from occurring during solvolysis. This laboratory has for several years been studying the kinetics of solvolysis reactions of complexes containing the tren ligand. Among these studies has been the examination of the primary acid hydrolysis [19] and the solvolysis in non-aqueous solvents [20] of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$. To further study the role of the solvent in the primary acid hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$, the kinetics were studied in acidic methanol– and ethanol–water mixtures of varying alcohol content. The rate constants were correlated to the bulk properties of the solvent, such as, mole fraction of alcohol, dielectric constant and ionizing power of the solvent.

Experimental

Materials

Methanol, ethanol and perchloric acid were all reagent grade. Anhydrous ethanol was produced by drying 95% ethanol over 3 Å molecular sieve statically. Conductivity grade water was prepared by doubly distilling deionized water in a glass still and then boiling for twenty minutes. Dichloro(2,2′,2″-triaminotriethylamine)cobalt(III) chloride hemihydrate, $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$, was synthesized according to the methods described by Liu [21].

Kinetic Methods

The kinetic techniques, *i.e.* thermostatting of cells and calculation of pseudo-first-order rate constants have been described previously [19]. The acid hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$ was performed in the following manner: Enough of the complex was weighed out in a 25-ml volumetric flask to result in an approximately millimolar solution of the complex. The solvent and the flask containing the complex were thermostatted to the desired temperature in a circulating water bath to ±0.2 °C. The solvent, containing 0.1 M perchloric acid, was rapidly added to the complex, diluting the complex to 25 ml. The ionic strengths of these solutions varied between 0.098 and 0.104 M. Approximately 0.75 ml of this solution was decanted into a pyrex cell of a 1 cm path length, which was thermostatted to ±0.2 °C of the desired temperature.

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When the solvents of the higher alcohol mole fraction were utilized, the solutions were decanted through a pyrex funnel containing glass wool which was at the desired temperature. The average time that elapsed before recording the absorbance was 30 s. The change in absorbance was followed with a Perkin-Elmer Model 559A UV–Vis spectrometer at 529 and 600 nm. These wavelengths gave the maximum absorbance difference between the reactants and products. The repetitive scans were performed on a Hewlett-Packard Model 8540A UV–Vis spectrometer between 400 and 700 nm. Infinite-time absorbances were determined experimentally and triplicate runs agreed within ±3%. The pseudo-first-order rate plots were linear for at least three half-lives.

Because the solubility of the Co(III) complex in the alcohol-rich solvents was poor, the determination of whether the reaction went to completion was done separately. A known weight of the complex in a 25-ml volumetric flask was dissolved in the alcohol-rich solvent at room temperature and the absorbance was determined after approximately 7–8 half-lives had passed. This absorbance was compared to a Beer's law plot of $[Co(tren)Cl(H_2O)]^{2+}$.

Spectra of $[Co(tren)Cl_2]^+$ were obtained in anhydrous methanol, anhydrous ethanol and concentrated hydrochloric acid between 400 and 700 nm to ascertain whether the alcohol was coordinating to the complex. Enough complex was weighed out in a 25-ml volumetric flask to result in an approximately millimolar solution of the complex. The complex was diluted to 25 ml with the solvent of interest and then placed into an ultrasonic bath at 60 °C for 10 min. The solution was then allowed to cool to room temperature and the spectrum was taken.

Results

Acid Hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$

The kinetics of the acid hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$ has been studied in methanol– and ethanol–water mixtures of alcohol mole fractions of 0.05, 0.10, 0.15 and 0.20 (Table I). Figure 1 shows typical changes in the visible absorption which accompany the acid hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$ in the alcohol mixtures investigated. The isosbestic points observed in these spectral scans (450 and 558 nm) agree with the isosbestic points predicted (454 and 554 nm) from the spectra of $[Co(tren)Cl_2]^+$ and $[Co(tren)Cl(H_2O)]^{2+}$ and are indicative of simple stereoretentive solvolysis in each case. The spectral scans also revealed that the d–d band was shifted to shorter wavelengths and higher molar absorptivity. The shift of the d–d band to shorter wavelengths would be expected for the replacement of chloride by water. The reaction was found to go to completion in all the solvents investigated. The pseudo-first-order plots were found to be linear over three half-lives for the reaction and the rate constants were identical, within experimental error, for the same reaction conditions at both 529 and 600 nm. The spectra of [Co(tren)-

TABLE I. The Acid Hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$ in Aqueous–Alcoholic Solvents

Co-solvent	Mole percent (%)	Rate × 10^3 (s^{-1})				
		25.4 °C	30.4 °C	35.4 °C	40.4 °C	45.4 °C
Methanol	0[a]	2.99	4.96	8.10	13.0	20.6
	5	2.92	4.71	7.87	13.0	
		±0.03	±0.03	±0.15	±0.2	
	10	2.76	4.50	7.58	12.0	
		±0.05	±0.05	±0.11	±0.2	
	15	2.56	4.22	6.94	11.0	
		±0.04	±0.02	±0.12	±0.1	
	20	2.27	3.75	6.27	10.0	
		±0.02	±0.02	±0.09	±0.2	
Ethanol	5	2.60	4.42	7.49	12.2	
		±0.09	±0.08	±0.07	±0.1	
	10	2.35	4.08	6.10	9.73	
		±0.04	±0.10	±0.11	±0.07	
	15		3.02	5.26	8.76	14.4
			±0.10	±0.09	±0.08	±0.0
	20		2.64	4.88	7.33	12.3
			±0.05	±0.03	±0.04	±0.1

[a] Rate constants were calculated utilizing a linear regression with the values from ref. 19.

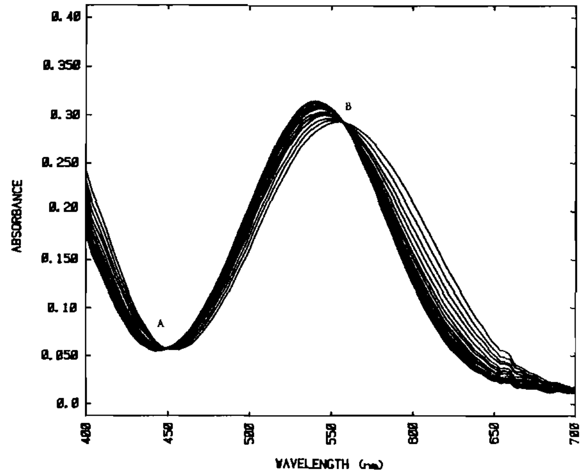

Fig. 1. Repetitive scans of the visible spectra from the acid hydrolysis of [Co(tren)Cl$_2$]Cl·$\frac{1}{2}$H$_2$O in 0.20 mole fraction of ethanol and 0.1 M HClO$_4$ at 30.4 °C. A, [Co(tren)Cl$_2$]$^+$; B, [Co(tren)Cl(H$_2$O)]$^{2+}$.

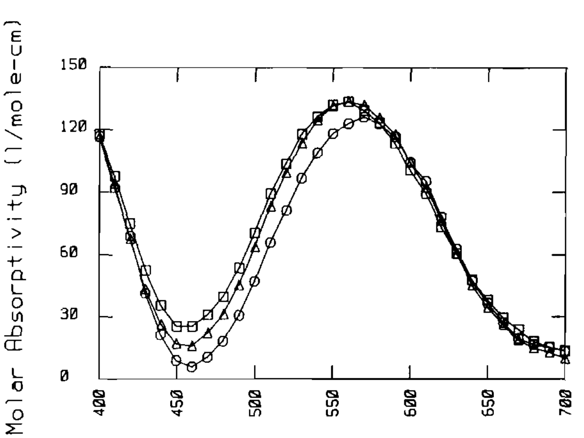

Fig. 2. Visible spectra of [Co(tren)Cl$_2$]Cl·$\frac{1}{2}$H$_2$O in anhydrous methanol (⊚), anhydrous ethanol (⊡), and concentrated hydrochloric acid (⚠).

Cl$_2$]$^+$ in anhydrous methanol, anhydrous ethanol and concentrated hydrochloric acid are given in Fig. 2. The spectra for the complex in anhydrous ethanol and concentrated hydrochloric acid appear identical within experimental error. The spectrum of the complex in anhydrous methanol shows a bathochromic shift with respect to the other two spectra. This indicates that under the conditions employed (60 °C with ultrasonic agitation for 10 min), the methanol is coordinating to the complex. The bathochromic shift indicates that methanol exerts a smaller effect on the crystal field splitting, resulting in a smaller crystal field splitting energy for the complex.

Because the rate constants were identical at both 529 and 600 nm and the isosbestic points in the spectral scans of the reaction in the water–alcohol mixtures agreed with those predicted from the spectra of [Co(tren)Cl$_2$]$^+$ and [Co(tren)Cl(H$_2$O)]$^{2+}$ it is concluded that there is no evidence for the solvolysis of the complex by the organic component in any of the solvent mixtures employed. This result is not surprising considering that the water was never present in less than a two-fold excess, and it is known to be about an order of magnitude more effective than alcohols in the solvolysis of the cobalt(III) ion. Thomas and Kane-Maguire [13] made similar conclusions in the aquation of bis(1,3-diaminopropane)cobalt(III) chloride in methanol– and ethanol–water mixtures.

Discussion

The existence of two isomers for the solvolysis products of [Co(tren)Cl$_2$]$^+$ has been well established [22–26]. The non-equivalency of the two *cis* positions has been proposed to be the result of the difference in the chemical environments of these positions [20, 23]. The position *cis* to the tertiary nitrogen of the tren ligand is in close proximity to several methylene hydrogen atoms, while the *trans* position is surrounded by amine hydrogens.

A polar molecule, such as water, bonded in the position that was *cis* to the tertiary nitrogen would be expected to result in repulsive interactions with the methylene chains of the tren ligand. These interactions would result in distortion of the amine, leading to an increase in the intensity of the $^1T_1 \rightarrow {}^1A_1$ transition. It has been argued that these repulsive interactions with a solvent molecule approaching the *cis* position would favor a dissociative (D) mechanism [20, 27] by preventing the solvent molecule from approaching the metal ion until the chloride ion had left. For a polar solvent molecule bonded in the position *trans* to the tertiary nitrogen, attractive interactions with the amine protons would not be expected to result in distortion of the amine. It has been suggested that the attractive interactions between a polar solvent molecule approaching the *trans* position and the amine protons would favor an associative (A) [27] mechanism, due to the increased interactions between the solvent molecule and the leaving chloride ion [20]. It is apparent from Fig. 1, that the product of the acid hydrolysis of [Co(tren)Cl$_2$]$^+$ exhibits a greater molar absorptivity than [Co(tren)Cl$_2$]$^+$. Therefore, we have tentatively assigned the chloride ion *cis* to the tertiary nitrogen as being replaced by a water molecule. This is consistent with a dissociative (D) process [20].

In Fig. 3, the dependence of the logarithm of the rate constant on the mole fraction of the alcohol is plotted. Non-linear behavior in the data can be observed for both of the alcohols used. This may be attributed to the selective solvation of the com-

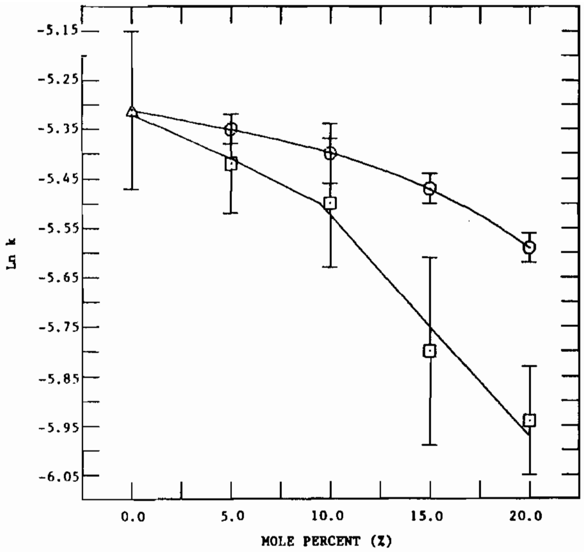

Fig. 3. Plot of the dependence of the logarithm of the rate constant on the mole fraction of co-solvent present of aqueous (△), aqueous methanol (⊙), and aqueous ethanol (⊡) solutions at 30.4 °C.

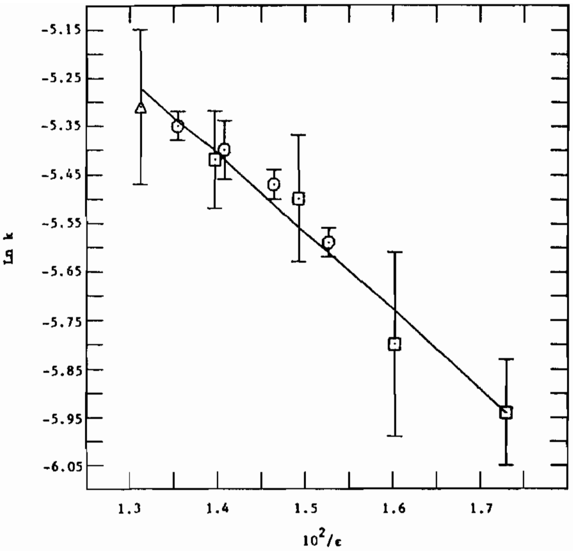

Fig. 4. Plot of the dependence of the logarithm of the rate constant on the relative dielectric constant of aqueous (△), aqueous methanol (⊙), and aqueous ethanol (⊡) solutions at 30.4 °C.

plex by water. The non-linear behavior found in Fig. 3 when ethanol was the co-solvent, is of interest because it appears to be related to the critical concentration of ethanol [1]. The correlation between the logarithm of the rate constant and the mole fraction of ethanol can be approximated by two straight lines that intersect at a mole fraction of ethanol of 0.09, which corresponds to the critical concentration of ethanol [1]. Below the critical concentration of ethanol, the ethanol molecules are able to occupy the interstitial sites in the water structure. In doing so monomeric water molecules are displaced from the interstitial sites. Therefore there are more water molecules and less ethanol molecules available for solvating the complex. After the critical concentration of ethanol is surpassed, the solvent structure collapses and the solvation sheath is expected to be similar to the bulk solvent. Burgess and Price [28] observed similar behavior in the aquation of *cis*-$[Co(en)_2Cl_2]^+$ in aqueous t-butyl alcohol. The authors found that the trend of the aquation rates of *cis*-$[Co(en)_2Cl_2]^+$ with solvent composition showed a marked change of direction at a t-butyl alcohol mole fraction of 0.035. They attributed this inflection to the structure-making and -breaking of the alcohol. These same investigators found that the aquation rate of $[Co(NH_3)_5Cl]^{2+}$ varied smoothly with the solvent composition of aqueous t-butyl alcohol solvents. This would indicate that the ethylenediamine (en) ligands or differences in the charges (+1 *versus* +2) had a significant role in the non-linear behavior of the rate of aquation of *cis*-$[Co(en)_2Cl_2]^+$ in aqueous t-butyl alcohol *versus* the solvent composition.

In Fig. 4, the dependence of the logarithm of the rate constant on the dielectric constant is linear, within experimental error, over all the solvents investigated [17]. The linear least-squares fit resulted in a linear plot with a correlation coefficient of −0.98. This would confirm the earlier observation made by Saliby and co-workers [20] that the solvolysis rate of $[Co(tren)Cl_2]^+$ was dependent on the dielectric constant of the non-aqueous solvent used.

For the solvolysis reactions of cobalt(III) and nickel(II) complexes, the Grunwald–Winstein equation [29], $\log k/k_0 = mY$, has been found to be linear for known dissociative reaction mechanisms [13, 15, 30–35]. The slopes of these plots have been found to vary between 0.09 to 0.36. These values of *m* are five times smaller than those for the analogous alkyl halide solvolysis reactions. This has been attributed to the greater ionic character of the Co–X (X = halide) bond relative to the C–X bond. This indicates that the increase in the anion solvation in the transition state, as compared to the ground state, is much higher in the case of the alkyl halide, leading to a greater ionizing power sensitivity in the dissociative solvolysis rates [31].

A non-linear least-squares fit of the logarithm of the rate constant *versus* the ionizing power of the solvent (Table II) for all the solvents investigated at 30.4 °C resulted in a second order polynomial with slopes varying from 0.14 to 0.73. In the range of *Y* values of 2.7 to 3.5, the Grunwald–Winstein plot for the aquation of $[Co(tren)Cl_2]^+$ in aqueous–methanol and –ethanol solvents is linear with a slope of 0.28. Burgess [34] has found that *cis*-$[Co(en)_2Cl_2]^+$ exhibits a linear behavior in the plot of the

TABLE II. Physical Properties of the Solvent *versus* the Logarithm of the Rate Constant at 30.4 °C

Co-solvent	Mole percent (%)	Relative dielectric constant (ϵ_r)	Solvation parameter $(Y)^b$	ln *k*
Methanol	0	76.2	3.49	-5.31^a
	5	73.8	3.27	−5.35 ±0.03
	10	71.0	3.03	−5.40 ±0.06
	15	68.3	2.79	−5.47 ±0.03
	20	65.5	2.54	−5.59 ±0.03
Ethanol	5	71.6	3.18	−5.42 ±0.10
	10	67.0	2.79	−5.50 ±0.13
	15	62.4	2.39	−5.80 ±0.19
	20	57.8	1.99	−5.94 ±0.11

[a]Value extrapolated from the data in ref. 19. [b]Extracted from ref. 37.

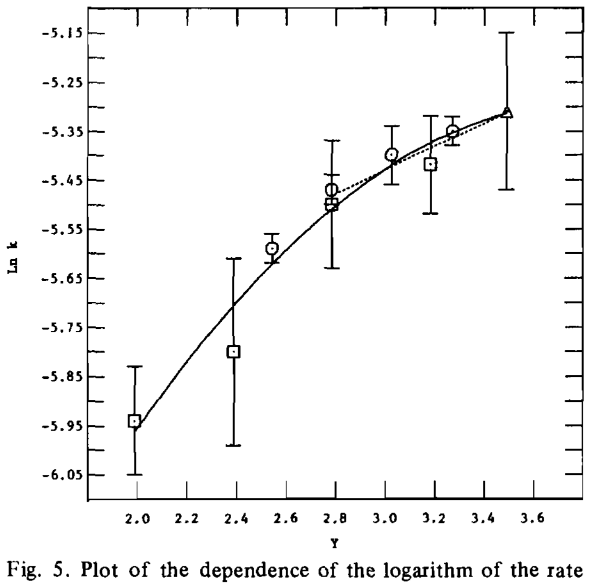

Fig. 5. Plot of the dependence of the logarithm of the rate constant on the solvation power of aqueous (△), aqueous methanol (○), and aqueous ethanol (□) solutions at 30.4 °C.

logarithm of the rate constant *versus* the ionizing power of the solvent in the aqueous–methanol and –ethanol solvents with a slope of 0.35 in the range of *Y* values of 2.7 to 3.5. The author did not investigate this aquation reaction in aqueous–methanol or –ethanol below a *Y* value of 2.7. It is proposed that the non-linear behavior of the Grunwald–Winstein plot (Fig. 5) is the result of interactions of the non-aqueous component of the alcohol with the methylene groups of the tren ligand. After the critical concentration of the alcohol is surpassed, the solvation sphere will reflect the same composition as the bulk solvent. The influence of ion-pairing on the rate of aquation of $[Co(tren)Cl_2]^+$ in the solvents containing the larger amount of alcohol would not appear to be significant enough to cause the non-linear behavior in the Grunwald–Winstein plot. Langford [35] reported a linear correlation between log *k* and *Y* in the aquation of *trans*-$[Co(en)_2Cl_2]^+$ in aqueous–methanol solutions up to 60% methanol by volume. Saliby *et al.* [20] found that the ion pairing constants, K_{IP}, were lower for $[Co(tren)Cl_2]^+$ than for the analogous bis(ethylenediamine) species [36] in dimethylsulfoxide and dimethylformamide solvents. The authors concluded that the carbon backbone of the tren ligand blocked the favorable site for ion pairing [20].

General trends in the thermodynamic parameters for the acid hydrolysis of $[Co(tren)Cl_2]^+$ in water–alcohol mixtures can be observed in Table III. For all the solvents investigated, the enthalpy is more positive in the transition state than in the reactants, whereas the entropy is slightly more negative in the transition state than in the reactants. This indicates that bond-breaking is more prominent than bond-formation, and that the amount of order is greater in the transition state. This is in accord with the assignment of a dissociative (D) reaction.

In summary, the solvolysis of $[Co(tren)Cl_2]^+$ in acidic aqueous–methanol and –ethanol solvents have been found to be acid hydrolysis reactions occurring via dissociative reaction mechanisms.

TABLE III. The Thermodynamic Activation Parameters for the Acid Hydrolysis of $[Co(tren)Cl_2]Cl\cdot\frac{1}{2}H_2O$ in Aqueous–Alcoholic Solvents

Co-solvent	Mole percent (%)	E_a	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$ (J/K mol)
		(kJ/mol)			
Methanol	0[a]		88	74	−44
	5	78 ± 3	88 ± 1	76 ± 3	−41 ± 14
	10	77 ± 4	88 ± 2	74 ± 4	−45 ± 19
	15	77 ± 3	88 ± 2	74 ± 3	−46 ± 16
	20	77 ± 3	88 ± 1	74 ± 3	−47 ± 13
Ethanol	5	77 ± 5	88 ± 2	74 ± 5	−47 ± 24
	10	74 ± 3	88 ± 2	71 ± 3	−56 ± 16
	15	83 ± 4	89 ± 3	81 ± 4	−27 ± 24
	20	77 ± 2	89 ± 2	75 ± 2	−40 ± 11

[a] Data taken from ref. 19.

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