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Substitution Reactions of Metallic Complexes of 2,2′,2″-Triaminotriethylamine. XVI. Kinetics of the (Oxalato)(2,2′,2″-triaminotriethylamine) Cobalt(III) Cation in Dilute and Concentrated Acid

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Abstract

The main emphasis in the study has been the investigation of the kinetics of the stepwise reactions of $[Co(tren)C_2O_4]^+$ ion [tren = 2,2′,2″-triaminotriethylamine, $N(CH_2CH_2NH_2)_3$] in both dilute and concentrated acids, as well as the characterization in solution of some new Co(III) tren complexes. The aquation reaction was conducted in 1.0 M $HClO_4$ solution under various conditions. Protonation of a carbonyl oxygen in the complex appeared to increase the lability of the Co–O moiety, leading to a unidentate oxalate ligand. The stepwise anation of $[Co(tren)C_2O_4]^+$ to $[Co(tren)Cl_2]^+$ in concentrated HCl was also followed. Both systems react by a dissociative reaction mechanism.

Introduction

In our laboratory, there have been numerous investigations based on reaction mechanisms of the octahedral cobalt(III) [2], chromium(III) [3] and rhodium(III) [4] complexes of the 2,2′,2″-triaminotriethylamine (tren) ligand. Our interest in the metal complexes of this ligand is derived from its resistance to isomerization, due to its tripodal nature. This report will focus solely on the reaction mechanisms of the oxalated tren complex of cobalt(III) under various conditions.

Saliby and Madan [3a, d] investigated the hydrolyses of $[Cr(tren)C_2O_4]^+$ in both dilute and concentrated acids. They also followed the stepwise aquation of $[Cr(tren)C_2O_4]^+$ to $[Cr(H_2O)_4C_2O_4]^+$ in dilute acid solutions, and the anation of $[Cr(tren)C_2O_4]^+$ to $[Cr(tren)Cl_2]^+$ in concentrated HCl. Pursuant to our interest in this area, we undertook the present kinetic study of the $[Co(tren)C_2O_4]^+$ complex under almost the same conditions as those of the chromium(III) analog. Generally, the cobalt(III) complexes react at a slower rate than that of their chromium(III) analogs. There are two reasons for this, one being the unavailability of d orbitals. Secondly, there is a greater loss in crystal field stabilization energy in forming the transition state for a d^6 cobalt(III) complex than there is for a d^3 chromium(III) complex.

The reactivities of $[M(en)_2C_2O_4]^+$ and $[M(C_2O_4)_3]^{3-}$ for cobalt(III) [5–7] and rhodium(III) [5, 8, 9] complexes in aqueous acidic solutions have all been broadly examined. It appears that there are two kinetically distinct types of coordinated oxygen. The rate and mechanism of dissociation of a bidentate oxalato chelate has been sparingly studied, except at elevated temperatures. Basolo and Pearson [10] in their report, gave an approximate value of $K_d \approx 10^{-10}$ s^{-1}. The oxalato group proved to be strongly bound to the central metal. Because of this, the variation of factors influencing metal–ligand strength would be likely to alter the reaction rates significantly [11]. In our case, the alteration in rate appears to be due to the peculiar geometry of the complex produced by the tren ligand. The $[Co(tren)C_2O_4]^+$ cation has a distorted octahedron, which would tend to expose the bidentate oxalato group more fully to solvent attack.

Experimental

Materials and Reagents

2,2′,2″-Triaminotriethylamine trihydrochloride (tren·3HCl) was prepared by the method of Paolette *et al.* [12]. The product was tested by titrimetric analysis, using $AgNO_3$ standard solution, and also by taking infrared spectra.

Dichloro(triaminotriethylamine) cobalt(III) chloride hemihydrate was prepared by the procedure used by Miller and Madan [13].

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Oxalato(triaminotriethylamine) cobalt(III) perchlorate: the compound [Co(tren)Cl_2]Cl (1.0 g) was dissolved in a small amount of water and added to 0.75 g of $Na_2C_2O_4 \cdot H_2O$. The mixture was heated on a steam bath for about 5 min, and the bright red solution was then decanted from the undissolved $Na_2C_2O_4 \cdot H_2O$, and $NaClO_4$ (0.45 g) was added. The red crystals were cooled and washed. The yield was about 68%. All other chemicals used for the study were reagent grade purity.

Infrared Spectra

The infrared spectra of the complexes were obtained from a Perkin-Elmer Model 283B recording spectrophotometer in the region of 250–4000 cm^{-1} using CsBr plates. The mulling agent employed was Nujol liquid. The values of complexes agreed with those obtained by Kuo *et al.* [14].

Electronic Absorption Spectra

Visible electronic absorption spectra were measured on two different recording spectrophotometers: a rapid-scanning diode-array spectrophotometer (Model HP-8450A) and a Beckmann DU spectrophotometer, with thermostated cell compartments. All measurements were done using 1 cm matched cells.

Kinetic Measurements

Aquation of [Co(tren)Ox]$^+$ in 1.0 M $HClO_4$ at 25 °C

When [Co(tren)Ox]$^+$ was dissolved in 1.0 M $HClO_4$, the spectral scans showed absorption maxima at $\lambda_{max} = 354$ and 496 nm. This was in good agreement with previously measured absorption spectra of the same compound in H_2O reported by Kuo *et al.* [14] (355 and 497 nm). The kinetic measurements were made spectrophotometrically using an HP-8450A model in matched quartz cells of 1 cm path length. The concentration of the reactants in all kinetic runs was within the range of $(1.0–1.5) \times 10^{-3}$ M. The reaction of [Co(tren)Ox]$^+$ was followed at a constant wavelength of 496 nm where the maxima differences in absorbance between reactants and products occur.

Anation of [Co(tren)Ox]$^+$ in 12 M HCl

The chosen wavelength for this kinetic study was 500 nm where the maxima molar absorptivity was 146 M^{-1} cm^{-1}. All kinetic measurements were obtained using a BECKMANN Du spectrophotometer with matched cells of 1 cm path length. The complex concentration range for the reactions was $(1.0–1.4) \times 10^{-3}$ M at different temperatures: 25, 35.5, 40, 44.9, 50 and 55 °C. The progress of the reaction was followed by measuring the change of absorbance at certain time intervals.

Results and Discussion

Aquation of [Co(tren)C_2O_4]$^+$ to [Co(tren)-$HC_2O_4(H_2O)$]$^{2+}$ and Ultimately to [Co(tren)$(H_2O)_2$]$^{3+}$ in 1.0 M $HClO_4$

For 15 min at 25 °C, during aquation, observable spectral changes occurred with the retention of isosbestic points at 350, 396.7, 466.8 and 547 nm. These points confirm the first aquation product of 2+ charge. Then, at prolonged elevated temperatures, this reaction can be forced to give a stable diaquo complex species and $H_2C_2O_4$. Dasgupta and coworkers [8] determined quantitatively the concentration of the released oxalate by precipitation and separation as CaC_2O_4, and by titration with standard $KMnO_4$ solution (from the aquated oxalated group of complexes). In our research, however, we used spectral studies to identify the diaquo complex, which agreed with results obtained by Miller and Madan [13] [354 nm ($\epsilon_M = 86$ M^{-1} cm^{-1}); 500 nm ($\epsilon_M = 88$ M^{-1} cm^{-1})].

The specific rate constants, k_{obs}, for the individual aquation reactions, determined by means of the spectrophotometric method under specified conditions, are given in Table I. The data show the salt effect and change of the ionic strength with respect to the rate constants at high ionic strength. The added electrolyte, $NaClO_4$, lowered the water activity.

TABLE I. Rates of Acid Hydrolysis of [Co(tren)Ox]$^+$ in 1.0 M $HClO_4$ Under Various Conditions at 496 nm

T (°C)	Ionic strength, μ	$10^3 \times k$ (s^{-1})
25.0	1.0	9.74 ± 0.04
28.8	1.0	11.23 ± 0.02
32.0	1.0	12.29 ± 0.01
36.2	1.0	13.94 ± 0.01
25.0	3.0[a]	9.25 ± 0.01
25.0	2.5[a]	9.61 ± 0.01
25.0	1.5[b]	10.00 ± 0.03

[a] Added electrolyte was $NaClO_4$. [b] Added electrolyte was Na_2SO_4.

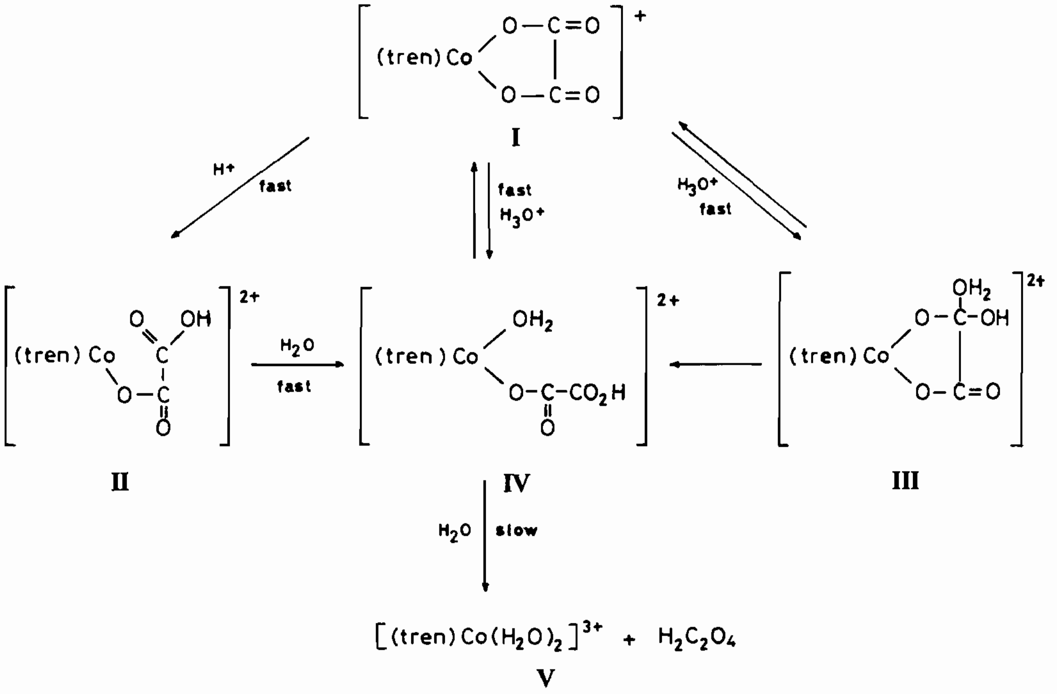
The Co(tren)C_2O_4]$^+$ cation is much more reactive than [Co$(en)_2C_2O_4$]$^+$ because of the geometry of the tren ligand, which allows a dissociative character for the former complex. This process, in the case of the tren complex, might be brought about by a drawing back of the bonds between the metal and the primary amine nitrogens towards the tertiary nitrogen atom, so as to 'make room' for the incoming water molecule to enter the coordination site. Consequently, there is a 'strain effect' on the complex, resulting in an increase in reactivity, as predicted by Crawford [15] in his system.

The lack of more specific information on rate constants and activation parameters for reactions of $[Co(en)_2C_2O_4]^+$ in acidic solution precludes a detailed comparison with $[Co(tren)C_2O_4]^+$. It is conceivable that as one moves from complexes of the type $[M(C_2O_4)_3]^{3-}$ to those of types $[M(en)_2C_2O_4]^+$ and $[M(tren)C_2O_4]^+$, one would expect differences between rhodium and cobalt to be accentuated. The more positive center for rhodium amine complexes in comparison to that for $[Rh(C_2O_4)_3]^{3-}$, enhances further the associative character of processes involving substitution at the metal center. But in the case of Co(III) amine complexes, compared to $[Co(C_2O_4)_3]^{3-}$, the change to the more positive metal center enhances the dissociative character for substitution processes at the Co(III) center [16]. This is due to the differences in crystal field stabilization energies of these metal ions.

Our studies in 1.0 M $HClO_4$ predict three possible pathways for the Co(III) complex kinetic mechanism. This is due to the probability that the 'outer oxygen-exchange' with solvent might proceed faster than the 'inner oxygen-exchange' with solvent. This interpretation is in good agreement with the inner/outer oxygen interchange mechanism suggested in the aquation of $[Rh(en)_2C_2O_4]^+$ [8], $[Co(C_2O_4)_3]^{3-}$ [7] and $[Co(en)_2C_2O_4]^+$ [5] complexes. These possible pathways for oxygen exchange and aquation are illustrated below.

The exchange of outer oxygen can take place without the need for ring opening, as indicated by path B. This path can lead to Co–O bond cleavage, followed by C–C bond rotation, which gives rise to the monodentate oxalato species (**IV**). The complete aquation to $[Co(tren)(H_2O)_2]^{3+}$ and oxalic acid was proven to occur by way of the monodentate oxalato species (**IV**), after prolonged heating at elevated temperatures. The observed rate constants and spectral studies fit the above mechanism, especially path B. This reasoning is in good agreement with the mechanism proposed by Chatterjee and Das [17] for the acid dissociation of malonato- and succinato-bis-(ethylenediamine) cobalt(III) systems. The other two paths proposed are less likely, but are probable at elevated temperatures. The proposal that **IV** species form by way of **II** species gives an implication that Co–O bond fission proceeds more rapidly than the outer oxygen exchange, which is not the case here. This is due to the thermodynamic stability of the $[Co(tren)HC_2O_4(H_2O)]^{2+}$ complex under our experimental conditions.

The activation parameters, given in Table II, provide an insight into the nature of the aquation of the $[Co(tren)C_2O_4]^+$ complex in 1.0 M $HClO_4$. They were derived from the Arrhenius plot of log k_{obs} *versus* $1/T$ (K^{-1}). The results favored a dissociative mechanism [18] as given in Scheme 1.



where path A is I → II → IV → V; path B is I ⇌ III → IV → V; and path C is I ⇌ IV → V.

TABLE II. The Thermodynamic Activation Parameters for the Aquation and Anation of $[Co(tren)Ox]^+$

	E_a	$\Delta G^{\#}$ (Kcal/mol)	$\Delta H^{\#}$	$\Delta S^{\#}$ (cal/K mol)
Aquation using 1.0 M $HClO_4$ at 25 °C	5.77 ±0.0	20.19 ±0.01	5.18 ±0.01	−50.37 ± 0.1
Anation using 12 M HCl at 25 °C	7.28 ±0.1	22.45 ±0.1	6.69 ± 0.1	−52.85 ± 0.1

$$[Co(tren)C_2O_4]^+ + H_3O^+ \xrightleftharpoons{K_a,\ \text{fast}} [Co(tren)HC_2O_4(H_2O)]^{2+} \qquad (1)$$

$$[Co(tren)HC_2O_4(H_2O)]^{2+} + H_3O^+ \xrightarrow{k_1,\ \text{slow}} [Co(tren)(H_2O)_2]^{3+} + H_2C_2O_4 \qquad (2)$$

Scheme 1.

Reaction (1) proceeds at a much greater rate than reaction (2), so no interference can be expected. Protonation of the carbonyl oxygen in the complex increases the lability of the Co–O moiety and leads to a unidentate oxalate ligand. It is thus conclusive that the effects of both chelate ring size and basicity of the leaving groups play a significant role with respect to the reactivity sequence.

Anation of $[Co(tren)C_2O_4]^+$ to $[Co(tren)Cl_2]^+$ in Concentrated HCl

The rates of reaction of the $[Co(tren)C_2O_4]^+$ complex in concentrated HCl under various conditions are given in Tables III and IV, and the activation parameters for the reactions are shown in Table II (as derived from an Arrhenius plot, Fig. 1).

TABLE III. Values[a] of k_{obs} (s^{-1}) for the Anation of $[Co(tren)Ox]^+$ in 12 M HCl at 500 nm

T (°C)	$10^4 \times k_{obs}$ (s^{-1})
25.0	2.13 ±0.02
35.5	3.18 ±0.02
40.0	4.04 ±0.02
44.9	4.65 ±0.03
50.0	5.50 ±0.05
55.0	6.51 ±0.20

[a] Correlation coefficient ranged between 0.98–1.0.

TABLE IV. Values of k_{obs} (s^{-1}) for the Second Reaction of $[Co(tren)Ox]^+$ in Concentrated HCl at 40 °C (λ = 500 nm)

$[H^+]$, M	$[Cl^-]$, M	$10^4 \times k_{obs}$ (s^{-1})
11.00	11.00	1.97 ± 0.01
11.00	11.50[a]	2.37 ± 0.02
11.00	12.00[a]	2.76 ± 0.02
11.75	11.75	3.37 ± 0.03
12.00	12.00	4.04 ± 0.02

[a] Adjusted with LiCl.

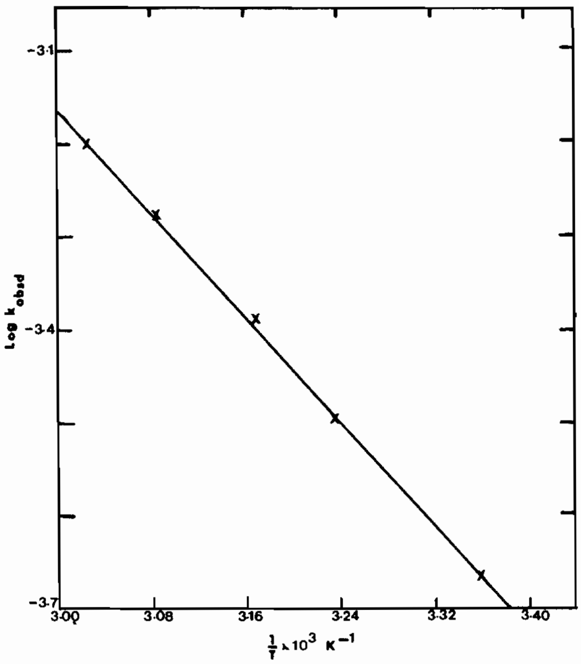


Fig. 1. Arrhenius plot for the anation of $[Co(tren)Ox]^+$ in 12 M HCl.

In 12 M HCl, $[Co(tren)C_2O_4]^+$ undergoes a series of Co–O bond rupture reactions which ultimately lead to the formation of the $[Co(tren)Cl_2]^+$ complex. Evidence for these reactions is provided by the shift of the d–d band maxima to higher wavelengths, the linearity of the pseudo-first order rate plots over three half-lives, and the formation of a violet $[Co(tren)Cl_2]^+$ complex product. The overall reaction can be outlined as follows:

$$[\mathrm{Co(tren)Ox}]^+ + \mathrm{H}^+ \overset{K_\mathrm{O},\text{ fast}}{\rightleftharpoons} [\mathrm{Co(tren)OxH}]^{2+} \xrightarrow[+\mathrm{Cl}^-]{k_\mathrm{Cl}} [\mathrm{Co(tren)OxHCl}]^+ \tag{3}$$

$$[\mathrm{Co(tren)OxHCl}]^+ + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} [\mathrm{Co(tren)OxH_2Cl}]^{2+} \xrightarrow[+\mathrm{Cl}^-]{k_\mathrm{Cl}^*} \underset{\text{(violet in color)}}{[\mathrm{Co(tren)Cl_2}]^+ + \mathrm{H_2Ox}} \tag{4}$$

Scheme 2. Proposed mechanism for the anation of $[\mathrm{Co(tren)Ox}]^+$ in concentrated HCl.

$$\underset{\text{(red)}}{[\mathrm{Co(tren)C_2O_4}]^+} + 2\mathrm{HCl} \longrightarrow \underset{\text{(violet)}}{[\mathrm{Co(tren)Cl_2}]^+ + \mathrm{H_2C_2O_4}}$$

The product was identified by taking its visible absorption spectra, which gave the band maximum at 556 nm ($\epsilon_M = 60.8\ M^{-1}\ cm^{-1}$). The final spectra were identical to those of the same complex determined by Madan and coworkers [2b].

The Co(III) complexes proved to react at a slower rate than their Cr(III) analogs, which is generally believed to be due to a greater loss in crystal fields stabilization for Co(III) complexes in forming the transition state. Another factor is the orbital extension, which is related to metal ion sizes. The filled d orbitals of the central metal ion for low spin complexes of Co(III) have room for extensions in the space around the metal, so the orbital overlapping influences the energy of the transition state.

The rates of the anation reactions of the first entry of the chloride ion into $[\mathrm{Co(tren)C_2O_4}]^+$ are found to be faster than those for $[\mathrm{Co(en)_2C_2O_4}]^+$. This appears to be due to different environments around the two coordinated oxygens of the oxalato group. These factors can be rationalized in terms of the geometry of the tren complex. This is due to the coordination site *trans* to the tertiary nitrogen, which is located in a hydrophilic pocket, while the other non-amine coordination site occupies the hydrophobic area. The hydrophilic pocket thus causes an increase in the rate, while the hydrophobic pocket reduces the entry of the chloride ion, as well as the hydrogen ion, in the anation reaction. This apparently leads to the slower rate of the second reaction (see Scheme 2), as compared to that of the ethylenediamine complex. The hydrophobic area is susceptible to repulsions from the aliphatic chains in the amine.

The detailed proposed mechanism of the anation of the $[\mathrm{Co(tren)C_2O_4}]^+$ complex has been outlined in Scheme 2. It was very difficult, for practical purposes, to study the first reaction step, because it proved to occur very rapidly. The kinetic data, given in Table IV, suggest that both the $[\mathrm{H}^+]$ and $[\mathrm{Cl}^-]$ contribute significantly to the rate expression for the second reaction. The consistency of the mechanism is shown by a rapid protonation equilibrium, followed by the rate-determining entry of a chloride ion. The second reaction, however, appears to be slower,

$$\begin{aligned}\text{rate} &= k_\mathrm{obs}[\mathrm{Co(tren)OxHCl^+}]\\ &= k_\mathrm{Cl}^*[\mathrm{Co(tren)OxH_2Cl^{2+}}][\mathrm{Cl^-}]\end{aligned} \tag{5}$$

and by rearrangement of eqn. (5), with respect to reaction mechanism (3) in Scheme 2

$$\begin{aligned}\text{rate} &= k_\mathrm{obs}[\mathrm{Co(tren)OxHCl^+}]\\ &= k_\mathrm{Cl}^*K_1[\mathrm{Co(tren)OxHCl^+}][\mathrm{H^+}][\mathrm{Cl^-}]\end{aligned} \tag{6}$$

this implies that

$$k_\mathrm{obs} = k_\mathrm{Cl}^*K_1[\mathrm{H^+}][\mathrm{Cl^-}] \tag{7}$$

Lewis and Randall [19] gave a simplified method of using activities rather than concentrations of the hydrochloric acid, which led to the reduction of eqn. (7) to

$$k_\mathrm{obs} = k_\mathrm{Cl}^*K_1 a_{\pm\mathrm{HCl}}{}^2 \tag{8}$$

Thus, a plot of log k_obs *versus* log $a_{\pm\mathrm{HCl}}$ gave a straight line of slope 2.09 ± 0.0, which is in good agreement with the theoretical value expected of slope 2.0, as illustrated on the plot of Fig. 2. This calculation supports the proposed mechanism.

Surprisingly, the values for the activation parameters for the aquation in 1.0 M $\mathrm{HClO_4}$ and the anation in concentrated HCl of the $[\mathrm{Co(tren)Ox}]^+$ complex were very similar, which proves the same trend of mechanism leads to the release of the oxalate ligand. The negative value for $\Delta S^\#$ indicates bond (order) strength brought by chelation of the tren and bidentate oxalate groups [20–22].

The above argument supports the explanation given by Taube and coworkers [5] for the acid-catalyzed exchange of bridging oxygen in $[\mathrm{Co(en)_2Ox}]^+$, and also by Broomhead and coworkers [21, 23] for the exchange between bridging oxygen and solvent water in $[\mathrm{Co(bipy)_2Ox}]^+$, which appeared very slow in reaction. They concluded, by comparison with other similar chelated complexes, that these types of oxygen exchange mechanism are due to different environments around the two coordinated oxygens of the oxalato group.

A comparative study of the results of both aquation and anation of the $[\mathrm{Co(tren)Ox}]^+$ complex in

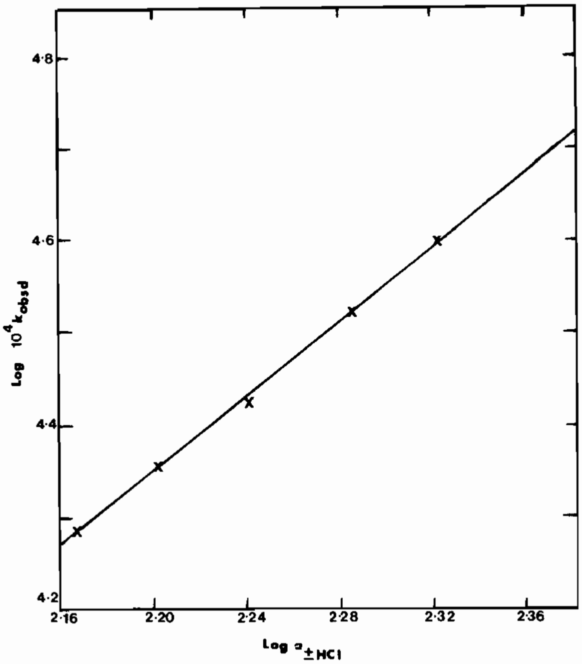


Fig. 2. Plot of log k_{obs} *vs.* log $a_{\pm HCl}$ for the second reaction of $[Co(tren)Ox]^+$ in HCl at 40 °C, λ = 500 nm.

dilute and concentrated acids indicates that the mechanisms involve the dissociative interchange mechanism. The rates with sterically-hindered ligands (without clear discrimination between incoming and leaving nucleophiles) can be explained as follows. The bond between cobalt and the leaving ligand is considerably stretched leading to Co–O bond rupturing, and the new bond between the metal and the entering ligand begins to form. In the same process, the geometric configuration seems to be retained because of strong chelation by the tren ligand. This is why, in the case of aquation, the Co–O bond rupturing became complete.

Conclusion

The present work suggests, in both cases, that the reactions occur in two stages. The first is the formation of a monodentate oxalato species, and the second is the complete loss of the oxalato group. The chemistry of the Co(III) systems was also found to be different from that of the Cr(III) systems. That can be justified on the basis of the ionic sizes and differences in crystal field stabilization energies.

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