PHOSPHATO AND RELATED BIS(TRIMETHYLENEDIAMINE) COBALT (III) COMPLEXES

(A mechanistic study in aqueous media)

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This thesis contains no material previously submitted for a degree or diploma in any University, and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

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SUMMARY

This thesis describes the preparation, structural and kinetic properties of the $(Cotn_2PO_4)^0$, $(Cotn_2(H_2O)PO_4)^0$ and $(Cotn_2(H_2O_2)^{3+}$ complex species.

The presence of bidentate phosphate in $(Cotn_2PO_4)^0$ is determined by infra-red studies. The stereochemical configuration of the monodentate phosphato species, $(Cotn_2(H_2O)H_2PO_4)^{2+}$, formed by dissolving the bidentate species in acid, is shown to be predominantly <u>cis</u> by UV-visible solution absorption spectral and proton magnetic resonance spectral studies.

A rapid and reversible equilibrium exists between the monodentate and bidentate phosphato cobalt (III) species in aqueous solution. The half times for this rapid interconversion are less than five minutes at 20.3°C. Significant concentrations of the bidentate species exist only within the pH range 5.5 to 8.5.

The ring opening reaction of the bidentate phosphato cobalt (III) species has been followed spectrophotometrically, in the pH range of 3 to 5, and the data satisfy the following rate expression

$$R_{ro} = k_{ro}{}^{0}\ (Cotn_2PO_4{}^{0}) + k_{ro}{}^{H^+}\ (Cotn_2PO_4H^+)$$

where $k_{ro}{}^{0}$ and $k_{ro}{}^{H^+}$ are 0.18 min^{-1} and 0.29 min^{-1} respectively at 20.3°C. At perchloric acid concentrations up to 2.5M, the rate constant, $k_{ro}{}^{H^{2+}}$, for the ring opening of the diprotonated bidentate, $(Cotn_2PO_4H_2)^{2+}$, is 77 min^{-1} at 10°C. A concerted mechanism involving

cis attack of water appears favourable for the acid catalysed paths for ring opening.

Release of the phosphato ligand from P^{32} labelled phosphato complex in acid and base media occurs relatively slowly. The acid hydrolysis reaction is at least 10^3 times slower than the ring opening reaction under the same conditions. The rate constants, k_1, k_2 and k_3, characterising the monoprotonated (P1), diprotonated (P2) and triprotonated (P3) species measured at 46.3°C are 3.1×10^{-2} min^{-1}, 0.2×10^{-2} min^{-1} and 18.3×10^{-2} min^{-1} respectively. The relative reactivities of the protonated species

$$P1 > P2 < P3 < P4$$

demonstrates the importance of protonation in influencing reactivity of a complex species. The P3 species exhibits a first order dependence on the activity of water and is probably hydrolysed via a mechanism involving S_N2 attack of water at the cobalt (III) centre.

In basic media, hydrolysis of the phosphato ligand from the monodentate complex proceeds via two paths, one independent of the hydroxide ion concentration and the other dependent linearly on the hydroxide ion concentration. The rate constants determined at 46.3°C for the uncatalysed and base catalysed paths are 2×10^{-2} min^{-1} and 14×10^{-2} min^{-1} respectively.

Ring opening and subsequent acid hydrolysis of the phosphato complex occur entirely by Co-O bond rupture as shown by O^{18}-studies.

The behaviour of the bis(trimethylenediamine) complexes is found to be very similar to their bis(ethylenediamine) counterparts. The increase in the ring size of the inert diamine ligands from five- to six-membered rings does not affect the rate of ring opening of the phosphato ligand. Hence, the rapid ring opening reactions of both bidentate phosphato complexes in the two systems may be attributed to the inherent strained nature of the four-membered phosphato chelate. However, the increase in the hydrolysis rates of the monodentate phosphato species to the corresponding diaquo species, for the bis(trimethylenediamine) system compared to the bis(ethylenediamine) system, (ten-fold for the mono- and di-protonated species, 160-fold for the triprotonated species, 70-fold and 30-fold via the base uncatalysed and base-catalysed paths respectively), appears to suggest that steric crowding plays a significant role in increasing these rates.

The instability of the six-membered trimethylenediamine chelate rings is shown by some investigations on the diaquo-bis(trimethylenediamine) cobalt (III) species.

CHAPTER 1

INTRODUCTORY SURVEY

1.1 Introduction

This thesis is concerned with substitution reactions of cobalt (III) complexes. Extensive studies of substitution reactions of octahedral complexes have been made, especially with complexes of cobalt (III) and chromium (III) because of their relative ease of preparation and slow rates of reaction. Taube[1] has classified metal complexes into two categories:

1) labile complexes are those whose reactions are complete within 1 minute at room temperature ($\sim$0.1M solutions of reactants)

2) inert complexes are those that react at rates too slow to measure or at rates that can be followed by conventional experimental techniques in time periods exceeding minutes.

In this study, some of the complexes undergo reactions within the time scale set by Taube[1] for 'labile' complexes whilst other reactions of the same or closely related complexes are much slower and these complexes would be described as 'inert'.

1.2 Substitution Reactions

Substitution reactions can involve either the replacement of one ligand by another in a complex or one metal ion by another. Using the Hughes and Ingold[2] convention these reactions can be described as nucleophilic substitution reactions, S_N, or electrophilic substitution reactions, S_E.

$L' + M - L \longrightarrow M - L' + L \quad S_N$

$M' + M - L \longrightarrow M' - L + M \quad S_E$

In this thesis the reactions are entirely of the S_N type.

In general, S_N replacement reactions can proceed via two main mechanistic pathways,

a) by the dissociative mechanism S_N1

b) by the displacement mechanism S_N2

An S_N1 reaction involves a two-step mechanism. The first step is a slow and rate determining unimolecular dissociation

$M\text{-}L \longrightarrow M + L$

followed by a rapid coordination reaction of M with another ligand, L'.

$M + L' \longrightarrow M\text{-}L'$

which competes with L (or the solvent) for reaction with M.

$L + M \longrightarrow M\text{-}L$

$S + M \longrightarrow M\text{-}S$

The intermediate metal complex, M, formed is of a reduced coordination number.

An S_N2 reaction involves a bimolecular rate determining step with an intermediate of increased coordination number.

$L' + M - L \longrightarrow L'\text{---}M\text{---}L \longrightarrow L'\text{-}M + L$

Because of the ambiguity of assignment of mechanisms due to the existence of borderline cases between S_N1 and S_N2, a further subdivision of these classifications[3] was made as shown in Table 1.1.

Table 1.1

Classification of Nucleophilic Substitution Reactions

S_N1(lim)	S_N1	S_N2	S_N2(lim)
	Degree of Bond Breaking in Rate Step		
Large	large	appreciable	none
	Degree of Bonding Making in Rate Step		
None	none to small	appreciable	large
	Evidence for Intermediate of Reduced C.N.		
Definite	indefinite	none	none
	Evidence for Intermediate of Expanded C.N.		
None	none	indefinite	definite

1.3 Rate Laws

Consider the reaction of a complex, RX, with a ligand, Y. A second order rate law, Rate = $k_2(RX)(Y)$, is consistent with one of the following two cases:

1) A bimolecular reaction (S_N2)

$$RX + Y \xrightarrow{k_2} RY + X$$

2) A rapid pre-equilibrium to R'X (a modified form of RX) followed by a bimolecular reaction

$$RX \overset{K}{\rightleftharpoons} R'X \quad \text{(rapid)}$$

$$R'X + Y \xrightarrow{k} RY \quad \text{(slow)}$$

$$\text{Rate} = k(R'X)(Y) = kK(RX)(Y) = k_2(RX)(Y)$$

In the anation reaction of aquo complexes

$$(RH_2O) + Y \longrightarrow (RY) + H_2O$$

a 5-coordinated intermediate may be involved

$$(RH_2O) \underset{k_2(+H_2O)}{\overset{k_1(-H_2O)}{\rightleftharpoons}} (R) \qquad \xrightarrow{\quad k\ (+Y)\quad} (RY)$$

A steady state treatment of this mechanism gives the rate law

$$\text{Rate} = \frac{d(RY)}{dt} = \frac{k_1k_3(RH_2O)(Y)}{k_2 + k_3(Y)}$$

At low (Y) where the pre-equilibrium is continuously maintained and $k_2 > k_3(Y)$, a second-order rate law will result.

$$\text{Rate} = k_3K(RH_2O)(Y)$$

where $K = \frac{k_1}{k_2}$. At high (Y), $k_3(Y) > k_2$ and the rate tends to

$$(\text{Rate})_{\text{lim}} = k_1(RH_2O)$$

It appears that the limiting rate of anation should become independent of the anion concentration if (Y) is sufficiently high. However, at high (Y), ionic association is serious and the rate of reaction may be determined by the ion pair so formed. An alternative mechanism, S_NIP (nucleophilic substitution ion pair), has been proposed.

$$R + Y \overset{K}{\rightleftharpoons} \underset{\text{ion pair}}{(R.....Y)}$$

$$(R.....Y) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (R'.....Y)$$

R' is a 5-coordinated species.

$$(R'.....Y) \xrightarrow{\quad k_3\quad} RY$$

$$\text{Rate} = \frac{k_1k_3K(R)(Y)}{k_2 + k_3}$$

Ion association is more marked in non-aqueous solvents of lower bulk dielectric constants than in water.

If RX has an acidic proton and Y is basic, a conjugate base equilibrium, K_{CB}, may be established.

$$RX + Y \xrightleftharpoons{K_{CB}} R'X + YH \text{ (rapid)}$$

$$R'X \xrightarrow{k} \text{products (slow)}$$

The rate may then be written

$$\text{Rate} = k(R'X) = kK_{CB}(RX)(Y)$$

$$= k_2(RX)(Y)$$

It is clear that a second order rate law may arise from a unimolecular rate determining step.

A first order rate law, Rate = $k_1(RX)$ for the reaction $RX + Y \longrightarrow RY + X$ may be consistent with either:

1) an S_N1 dissociation

$$RX \longrightarrow R + X \quad \text{(slow)}$$

$$R + Y \longrightarrow RY \quad \text{(fast)}$$

2) a bimolecular solvolytic reaction, in excess solvent

$$RX + S \longrightarrow RS + X \quad \text{(slow)}$$

$$RS + Y \longrightarrow RY + S \quad \text{(fast)}$$

In the interpretation of rate data, it is often useful to study the effect of temperature on the rate of reaction. The transition state theory expresses a second-order rate constant (in $M^{-1}sec^{-1}$) by the equation

$$k = K\frac{k'T}{h}\, e^{\Delta S^{\neq}/R}\, e^{-\Delta H^{\neq}/RT}$$

where K is the transmission coefficient, k' is the Boltzmann constant, h is Planck's constant, $\Delta S^{\neq}$ (cal $deg.^{-1}$ $mole.^{-1}$ or e.u.) is the entropy of activation, and $\Delta H^{\neq}$ (cal.$mole^{-1}$) is the heat of activation. $\Delta H^{\neq}$ is given by $(E_a - RT)$, where E_a is the activation energy. The transmission coefficient, K, is normally taken to be unity in the calculation of $\Delta S^{\neq}$.

The activation energy, E_a, may be evaluated using Arrhenius equation:

$$k = A\ e^{-E_a/RT}$$

where A is the Arrhenius frequency factor.

The entropy of activation measures the change in the entropy of the two reactants, as well as the change in entropy of the solvent, on formation of the transition state.

The heat of activation is the energy required to bring charged reactants up to each other, together with the energy required for the internal rearrangement of bonds within the reactant molecules.

It must be borne in mind that although observed values of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ often serve as a useful guide for deducing a reaction mechanism, they do not give clear cut evidence for a particular reaction mechanism because of the present doubtful understanding of the transition state.

Sometimes the effect of external pressure on the rate of reaction given by the relation

$$\ln\frac{(k_2)}{(k_1)} = -\frac{\Delta V^{\neq}(P_2 - P_1)}{RT}$$

is studied.

The volume of activation, $\Delta V^{\neq}$, which measures the change in partial molar volume when the reactants are converted to the transition state, may be used to elucidate the nature of the activation step, especially the degree of polarity of the activated complex.

1.4 General Influence of Solvents

The solvent plays an important role in the kinetic studies of a reaction. The interaction between the solvent and the reactants, activated complex or products can depend on the physical and/or chemical properties of the solvent. Water dissolves most metal complexes and is usually used as the solvent for the kinetic studies of the reactions of cobalt (III) complexes. In view of this, the properties of water that affect the interpretation of these kinetics will be briefly discussed.

First the structural properties of water will be considered.

1) In aqueous media, transitional metal cations are aquo complexes i.e. water molecules or ligands are coordinated to the metal ion. Hence, any reaction represented thus

$$M + L \longrightarrow ML$$

involves the replacement of a water ligand by L.

2) Metal ions that do not exert their maximum coordination number may have water weakly coordinated to them which may modify their stereochemistry and lability. This is especially important in square planar complexes.

3) Water may be incorporated by dipolar attraction into the structure of a cationic complex and markedly alter its reactions.

4) Water can hydrogen bond with ligands and enhance their removal during aquation.

There are two important kinetic effects of solvent water.

1) Being a strong nucleophilic, water may form an aquo complex in an intermediate step in the replacement of one ligand by another in a complex.

2) Water and its conjugate base, the hydroxide ion, can participate in the acid-base equilibria involving complexes to form new species which may be more reactive than the original ones.

1.5 Factors influencing the rate of substitution reactions

There are various factors that may affect the substitution rates and these are listed below:

1) The hydrogen ion concentration.
2) The central metal atom.
3) The displaced ligand.
4) The net charge on the complex.
5) The influence of π-bonding.
6) The electrical character of neutral ligands.
7) Geometrical isomerism.
8) Chelation.
9) The size of neutral ligands.

10) Isomerism of neutral ligands.

11) The solvent.

Basolo and Pearson[3], Stranks[4], and Langford and Gray[5] have discussed the effects of these factors extensively.

In this work, the substitution reactions of interest are the ring opening, chelation, acid and base hydrolyses and anation reactions of a typical cobalt (III) phosphate complex. The general aim is to study the effect of increasing the size of the neutral ligand on the rates of these substitution reactions. Pearson et al[6 7] studied steric effects of neutral ligands in the reactions of the series of complexes, <u>trans</u>- $Co(AA)_2Cl_2^+$ (AA = a bidentate diamine ligand). A summary of their results for the substitution of the first chloride by water is given in Table 1.2. There is a marked acceleration in rates with increasing replacement of the hydrogen atoms of the methylene groups by methyl groups. This strongly suggests a dissociative mechanism as repulsion and distortion of the ligands in a sterically crowded complex make it unstable. An even greater acceleration ($x10^3$) is observed by enlarging the ring from five to six members with insertion of another $-CH_2-$ group. Unfavourable bond angles appear to be forced on the six-membered ring. Hence the dissociation of one ligand will enable the ring to adopt a configuration of lower energy. It appears from Table 1.2 that the effect of increasing the size of the inert ligand on the rates of hydrolysis is due partly to the differences in activation energies, as offset by changes in activation entropies.

Table 1.2

Rates of acid hydrolysis of trans- $Co(AA)_2Cl_2^+$ at 25°C and pH 1.

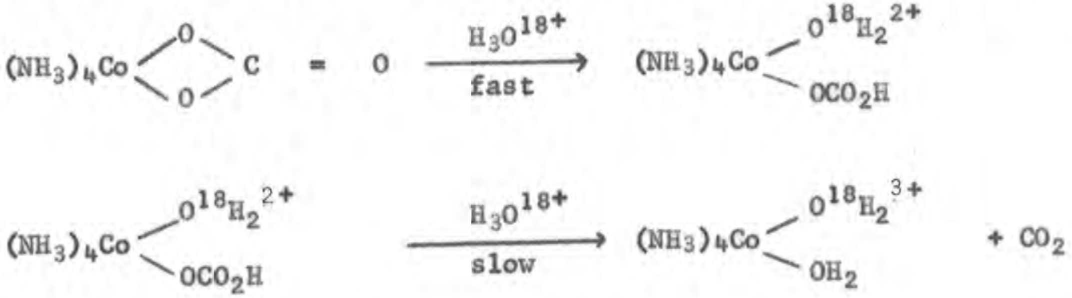
AA	$k_1 \times 10^3$ min^{-1}	E_{act} kcal.mole^{-1}	$\Delta S^{\neq}$ e.u.
$H_2N-CH_2CH_2-NH_2$	1.9	27	+9
$H_2N-CH_2-CH(CH_3)-NH_2$	3.7	28	+14
dl-$H_2N-CH(CH_3)-CH(CH_3)-NH_2$	8.8	26	+7
meso-$H_2N-CH(CH_3)-CH(CH_3)-NH_2$	250	24	+9
$H_2N-CH_2CH_2CH_2-NH_2$	600 (10°C)	-	-
$H_2N-C(CH_3)_2-C(CH_3)_2-NH_2$	instantaneous	-	-

1.6 Substitution Reactions involving oxyanions

Oxyanions such as CO_3^{2-}, $C_2O_4^{2-}$, $CH_2.C_2O_4H^-$, SeO_4^{2-}, SO_4^{2-} and PO_4^{3-} have been reported to act as monodentate and bidentate ligands in octahedral cobalt (III) complexes. The aquo-oxyanion complexes of the general formula $(CoN_4(H_2O)\ XO_4)$ where $XO_4 = SO_4^{2-}$, SeO_4^{2-}, or PO_4^{3-}, have been isolated.

The carbonato complexes, $(Co(NH_3)_5CO_3)^+$[8; 19] $(Co(NH_3)_4CO_3)^+$,[9] $(Coen_2CO_3)^+$[10] and $(Cotn_2CO_3)^+$[11] in their exchange reactions with free carbonate ion seem to suggest direct substitution in cobalt (III) complexes. However, it has been shown by O^{18} tracer studies[13,14] that in excess acid, the hydrolysis (or aquation) of $(Co(NH_3)_5CO_3)^+$ proceeds via C-O bond cleavage as in a decarboxylation reaction. Kinetic studies[12] on the $(Co(NH_3)_5CO_3)^+$ complex reveal that the reacting species is the bicarbonato complex, $(Co(NH_3)_5CO_3H)^{2+}$.

Similar isotopic studies on the tetrammine carbonato complex, $(Co(NH_3)_4CO_3)^+$ [15] appear consistent with the reaction scheme.



where the first step involves a rapid rupture of the Co-O bond. Conductivity measurements and studies of isotopic effects[16-21] indicate that the monodentate aquo carbonato complexes of cobalt (III), $(Co(NH_3)_4(H_2O)CO_3)^+$ and $(Coen_2(H_2O)CO_3)^+$, can exist substantially in aqueous solution. Boyle and Harris[11], attribute the slow rate of exchange of $(Cotn_2CO_3)^+$ with carbonate ion to steric hindrance which reduces the probability of direct exchange as well as lessens the amount of complex existing in the monodentate form, $(Cotn_2(H_2O)CO_3)^+$. Since the aquation of the monodentate carbonato complexes involves C-O bond cleavage as in a decarboxylation reaction[13 15 22], it is doubtful that this gives unequivocal proof for direct substitution in cobalt (III) complexes.

Andrade and Taube[23] have shown that the aquation of the oxalato-pentaammine cobalt (III) complex $(Co(NH_3)_5C_2O_4H)^{2+}$, proceeds via three parallel paths

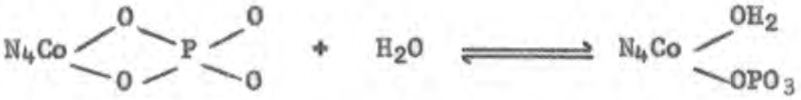
$k_o((NH_3)_5CoC_2O_4{}^+) + (k_1 + k_2(H^+))((NH_3)_5CoC_2O_4H^{2+})$

The position of bond cleavage was not reported.

The hydrolysis of the sulphato bis(ethylenediamine) cobalt (III) complex, $(Coen_2SO_4)^+$, has been investigated by Barraclough and Murray[24]. A limited study of the hydrolysis was done owing to the insolubility of the complex in solutions of ionic strength, $\mu > 0.2$. In pH < 5 no acid catalysis was shown for the hydrolysis of $(Coen_2SO_4)^+$ to $(Coen_2(SO_4)(H_2O))^+$. Salts of the aquosulphato cation, $(Coen_2(SO_4)(H_2O))^+$, have been prepared. The bidentate complex, $(Coen_2SO_4)ClO_4$ can only be obtained by heating the aquo-monodentate sulphato complex in the solid state in the absence of water solvent. There is, however, no evidence that the bidentate species can persist in aqueous solution in measurable concentrations.

Difficulty has been encountered by early workers[25-27] in synthesising phosphato-metal complexes in which the phosphate is directly coordinated to the metal ion. Von Siebert[28] has more recently prepared $(Co(NH_3)_4.PO_4).2H_2O$ and $(Co(NH_3)_4.H_2O.HPO_4).ClO_4.2H_2O$ where the ortho-phosphate ligand is presumably coordinated to the cobalt (III) via oxygen as a bidentate and as a monodentate ligand respectively. Schmidt and Taube[29] have isolated the crystalline complex, $(Co(NH_3)_5PO_4)2H_2O$ and generated the cations $(Co(NH_3)_5PO_4(CH_3)_3)^{3+}$ and $(Co(NH_3)_5PO_4(CH_3)_2)^{2+}$ in aqueous solution. Lincoln[30] has successfully synthesised the $(Coen_2PO_4)^0$ and $(Coen_2(H_2O)HPO_4)ClO_4$ complexes.

The phosphato-cobalt (III) complexes are unique in that an equilibrium exists between the bidentate and monodentate species in aqueous solution.

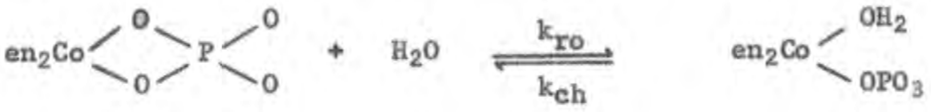


where $N_4 \equiv (NH_3)_4$ or $(en)_2$. This reversible equilibrium is established comparatively rapidly.

Lincoln and Stranks have established the stereochemical and the equilibrium hydrolytic properties[31] of complexes in which the ortho-phosphato ligand may coordinate either as a bidentate or a monodentate ligand. A lack of knowledge of these equilibrium and hydrolytic properties was probably the main cause of the difficulties met by the earlier workers in their attempts to prepare phosphato-metal complexes. Since the $(Coen_2PO_4)$ and $(Coen_2(H_2O).HPO_4)ClO_4$ species are less susceptible to basic decomposition than their ammine analogues and possess desirable solubility characteristics, they are ideally suited for the kinetic studies of ring opening[32], ring-closing[32], hydrolysis[33] and anation[35] reactions. The $(Co(NH_3)_4PO_4)^0$ species is only sparingly soluble in water.

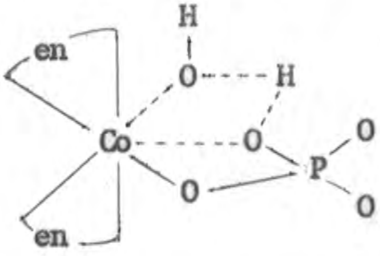
It was shown for the $Coen_2PO_4$ system that within a limited pH range of 5.5 to 7.5, 85% of all phosphate was coordinated to the cationic cobalt (III) species[31]. The infra red spectra of $(Coen_2PO_4)^0$ and $(Co(NH_3)_4PO_4)^0$ were consistent with a bidentate phosphato structure and that of $(Co(NH_3)_5PO_4)$ and $(Co(NH_3)_4(H_2O).HPO_4)^+I^-$ appeared consistent with a monodentate phosphato structure. PMR studies showed that the aquo phosphato complexes have the cis configuration predominantly.

The bidentate complexes persist in significant concentrations only in the range pH 5.5 to 7.5. The ring opening of the bidentate phosphato ligand is both acid and base catalysed. For the $Coen_2PO_4$ system, the half-times of the chelation and ring-opening reactions range from 2 minutes to 2 hours, at 22.5°C.



Ring opening of $(Coen_2PO_4)^0$ proceeds entirely by Co-O bond cleavage but at pH 6.8 and in 0.25M NaOH, 60-65% Co-O bond cleavage and 30-35% P-O bond cleavage occurs.

The rate of chelation of the monodentate phosphato complexes is less for the protonated species, $(Coen_2(OH)HPO_4)^0$ and $(Coen_2(OH_2)HPO_4)^+$ ($k_{ch} = 5.0 \times 10^{-2}\ min^{-1}$ and $1.3 \times 10^{-2}\ min^{-1}$ respectively), than for the non-protonated species[32] $(Coen_2(OH)PO_4)^-$ ($k_{ch} \leq 1 \times 10^{-3}\ min^{-1}$). The cis $(Coen_2(OH)OPO_3H)^0$ species chelates at a rate very similar to the rate of water exchange ($k_{ex} \approx 5.0 \times 10^{-2}\ min^{-1}$) for the hydroxyaquo species, cis-$(Coen_2(OH)OH_2)^{2+}$. Hence the basic phosphato ligand functions rather like the -OH basic ligand in promoting water exchange, via intramolecular hydrogen bonding. This function is decreased as additional protons are added to the phosphato ligand and it is a water ligand which is released on chelation. The proposed transition state[32] for ring opening and closing of $Coen_2PO_4{}^0$ was

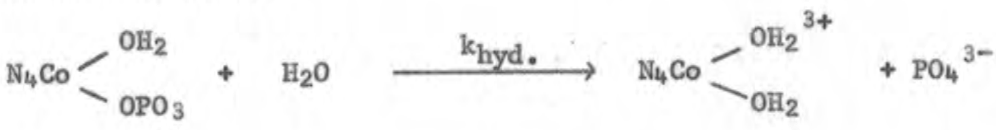


Recently, Huckital and Taube[65] prepared the monodentate malonato chromium (III) complex, $((H_2O)_5Cr - OOC.CH_2.COOH)^{2+}$ by the oxidation of chromium (II) by lead (II) in the presence of malonic acid. The rate of chelation of the complex at 25°C was found to increase with acid concentration according to the relation:

$$k(sec^{-1}) = 4.0 \times 10^{-6} + 2.2 \times 10^{-7}(H^+)$$

The first term in the rate law is similar to the rate constant for exchange of $Cr(OH_2)_6{}^{3+}$. Since the free carboxylato group is protonated, the second term in the rate law suggests that ring closure may proceed involving substitution at carbon rather than rupture of a chromium-water bond. This behaviour is quite distinct from the monodentate phosphato cobalt (III) complex.

The acid and base catalysed hydrolysis of the aquo phosphato cobalt (III) complexes proceed comparatively slowly (half-times of reaction range from hours to minutes within the temperature range of 45°C to 70°C).



$$N_4Co\genfrac{}{}{0pt}{}{OH_2}{OPO_3} + H_2O \xrightarrow{k_{hyd.}} \left(N_4Co\genfrac{}{}{0pt}{}{OH_2}{OH_2}\right)^{3+} + PO_4{}^{3-}$$

The reaction occurs entirely by Co-O bond rupture.

There is little kinetic evidence for or against the participation of water in the transition state in a hydrolysis reaction since most of the reported hydrolysis studies must be done under conditions in which the activity of water remains virtually constant. In concentrated acid solvents, large changes in water activity occur and there is significant protonation of the ligands. Some acid catalysed aquation reactions of cobalt (III) bis(ethylenediamine) complexes have been investigated by Staples[37-39], and Lambert and Mason[40 41] recently.

The monodentate phosphato ligand in the $(Co(NH_3)_5PO_4)$, cis-$(Co(NH_3)_4(OH_2)PO_4)$ and cis-$(Coen_2(H_2O)PO_4)$ complexes exhibits four degrees of protonation in perchloric acid.[31] The observation made by Lincoln and Stranks[33] that the rate of hydrolysis of the triprotonated phosphato complexes depends linearly upon the activity of water appears to be the first unambiguous evidence for direct attack of water at a cobalt (III) centre in a hydrolysis reaction. The effect of the successive protonation upon the lability of the phosphato ligand have at the same time been investigated. These acid catalysed hydrolysis reactions proceed via Co-O bond cleavage.

The selenato complex, $Coen_2SeO_4$,[42] shows a similar acid dependence to the phosphato complexes for its hydrolysis reactions. It is, therefore, not unreasonable to assume that the reaction will occur with Co-O bond rupture.

Base hydrolyses of the monodentate phosphato complexes proceed via two pathways; one, in which there is no base catalysis and the other, in which the reaction is base catalysed. For these base hydrolysis reactions, the Co-O bond is also severed.

In the anation reaction of $(Coen_2(OH_2)_2)^{3+}$ by PO_4^{3-}, a rapid equilibrium for the formation of ion pairs is first established, followed by a slower substitution step. Kinetic studies[35] have demonstrated that the anation reaction proceeds predominantly via the trans $(Co(en)_2(OH)OH_2)^{2+}.HPO_4^{2-}$ ion pair. For the anation of $Coen_2(OH_2)_2^{3+}$ by the sulphate ion, SO_4^{2-}, it was shown that the reaction involves the $Coen_2(OH_2)_2^{3+}.SO_4^{2-}$ ion pair predominantly[42].

1.7 Object of this Research

The main interest in this work is to examine the effects of increasing the ring size of the inert ligand from a five-membered ring, in the case of the ethylenediamine ligand, to a six-membered ring, in the case of a 1, 3 diaminopropane (or trimethylenediamine) ligand. The insertion of this additional $-CH_2-$ group in the ring introduces considerable steric crowding in the metal complex. Whereas the five-membered rings are almost planar in the $Coen_2PO_4$ complex, the six-membered rings in $Cotn_2PO_4$ are more puckered (Diagrams I and II). The ethylenediamine chelate rings in octahedral complexes can exist either in the envelope or gauche conformations.

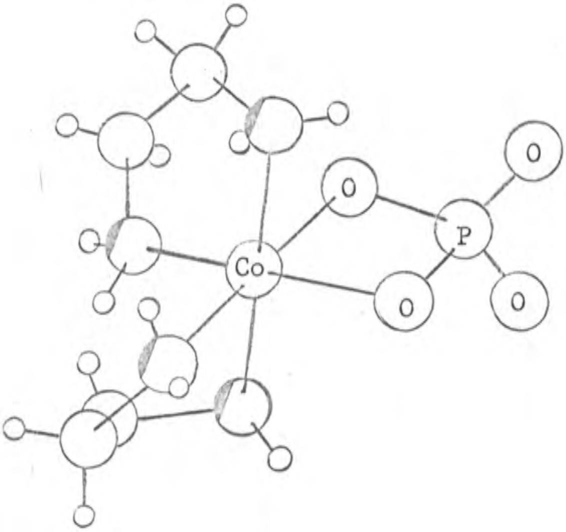


Diagram I $Coen_2PO_4$

○ Hydrogen

◯ Carbon

◐ Nitrogen

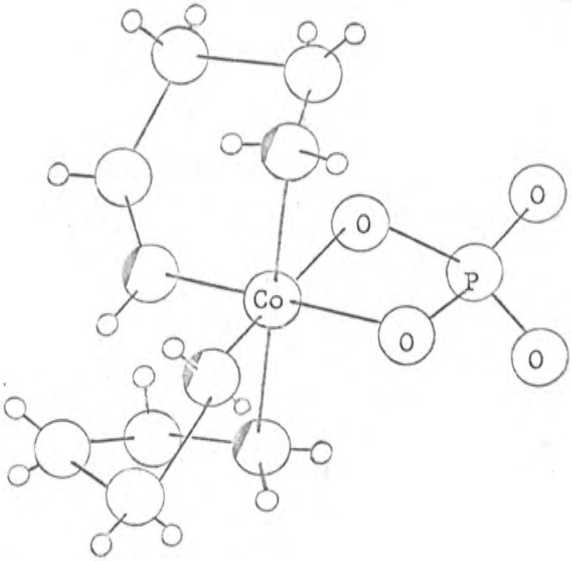
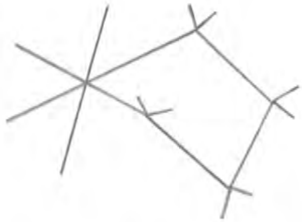
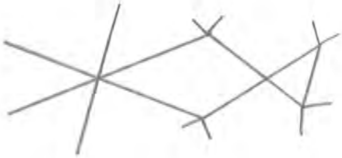


Diagram II $Cotn_2PO_4$



ENVELOPE STRUCTURE



GAUCHE STRUCTURE

The trimethylenediamine chelate ring may have one of the following conformations (i) chair (ii) boat (iii) skewboat. It can be shown with atomic models that the 'chair' configuration is highly improbable because of the many interactions between atoms and bonds. In the 'boat' arrangement some interactions between atoms do occur as shown in Diagram III such as interactions between the hydrogen atom on nitrogen (N_1) and the carbon atom (C_3); the C_1-hydrogen atom and C_2-hydrogen atom; the N_1-hydrogen atom and the C_3-hydrogen atom. If the diamine ring below the cobalt metal centre is inverted as shown in Diagram IV, the hydrogen-hydrogen interactions are removed but interaction with the lone pairs on the oxygen atom of the phosphate group is introduced. The configuration with minimum interaction appears to be the skewboat conformation as illustrated in Diagram II.

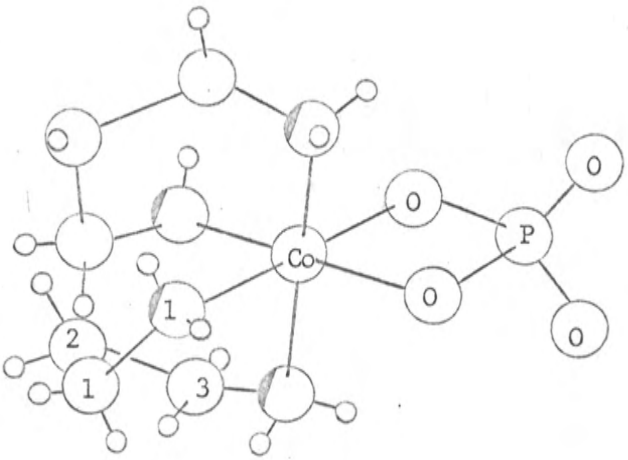


Diagram III Cotn$_2$PO$_4$ (boat)

○ Hydrogen

◯ Carbon

◐ Nitrogen

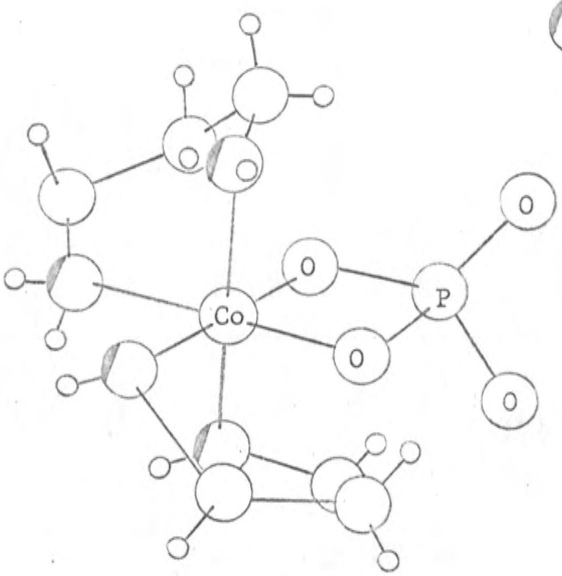
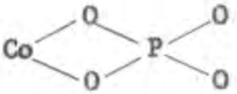


Diagram IV Cotn$_2$PO$_4$ (boat)

It may be further shown with the aid of atomic models that, with the ring opening of the phosphato ligand and introduction of an aquo ligand cis- to the monodentate phosphato ligand the situation of atomic interactions is not improved with six membered inert chelate rings. The aquo phosphato complex is just as sterically crowded as in the bidentate phosphato complex.

The inherent lability of the bidentate phosphato ligand in these complexes is presumably due to the strained character of the four membered ring formed by the phosphato group coordinated to the cobalt metal ion via two oxygen atoms. The phosphate ion on coordination assumes a distorted tetrahedral arrangement.



This work involves the preparation and the study of the kinetics of the phosphato (bistrimethylenediamine) cobalt (III) complex. It has been observed that complexes with six membered chelate rings are much less stable than those with five-membered rings, unless part of an aromatic system[43]. The reason for the instability lies in the 90° bond angles which are necessarily formed by metal chelate bonds. Release of one group from the octahedron and expansion of this bond angle will relieve the strain in the complex with a six membered ring. The presence of the trimethylenediamine in place of the ethylenediamine in cobalt (III) complexes gives rise to changes which appear to depend upon strains in the molecule rather than upon the strength of the cobalt-nitrogen link.

For a dissociative mechanism, S_N1, where the removal of a group would release the strain due to over crowding around the cobalt ion, an increase in the rate of hydrolysis would be expected. On the other hand, a decrease in rate would be expected for a displacement mechanism, S_N2. Due to steric hindrance, it would be more difficult to form a seven coordinated intermediate, therefore a fall in the rates of hydrolysis should be observed.

Like the ethylenediamine system, the phosphato bis(trimethylenediamine) complex has been shown to exist in both the monodentate and the bidentate form. The relative stability of these two forms are also studied in the pH range of 3 to 5. The instability of the six membered trimethylenediamine chelate rings is shown in some investigations on the diaquobis(trimethylenediamine) cobalt (III) system. Throughout this thesis the symbol 'tn' will be used to represent the trimethylenediamine (or 1,3 diaminopropane) ligand.

CHAPTER 2

METHODS OF PREPARATION AND ANALYSIS

2.1 PREPARATION

2.1.1 Trans - Dichlorobis (trimethylenediamine) cobalt (III) perchlorate

This complex was prepared by a slight modification of the method used by Bailar and Work to prepare trans - $(\mathrm{Cotn_2Cl_2})\mathrm{Cl}$.[44]

To anhydrous cobalt (II) chloride (6.9g.) in absolute alcohol (500ml.), distilled 1,3-diaminopropane (5.95g.) was added. Oxygen was bubbled through the mixture for 14 hours when the dull green solid so obtained was filtered and redissolved in a minimum volume of water. The mixture was filtered to remove unreacted cobalt (II) chloride and any cobalt oxide that might have formed. To the filtrate, concentrated perchloric acid (50ml.) was added and cooled in the refrigerator overnight. Dark green dichlorobis (trimethylenediamine) cobalt (III) perchlorate crystallised and was collected, washed with alcohol and then with acetone and air dried in a vacuum desiccator. The mother liquor was concentrated and cooled whence a second crop of crystals was collected. The total yield of complex was 34%.

2.1.2 Phosphatobis (trimethylenediamine) cobalt (III)

Dichlorobis (trimethylenediamine) cobalt (III) perchlorate (10g.) was slurried with aqueous trisodium phosphate (10g.). To the green slurry, water (40ml.) was added and the mixture was heated on a steam-bath until a crimson solution was formed. The pH of the solution was then adjusted to about 8 with a few drops of orthophosphoric acid. The resulting solution was concentrated by further heating. After cooling, the solution was filtered and sufficient ethanol was added to induce precipitation of the complex. After standing in a refrigerator overnight, the crystals were collected and recrystallised by dissolving in a minimum amount of water. After filtering this solution, an equal volume of 0.88 ammonia was added, followed by sufficient alcohol to fractionally precipitate the free phosphate as ammonium orthophosphate which was filtered off. To the filtrate more alcohol was added to precipitate the complex which was then collected. This process was repeated until all the excess phosphate had been removed as tested by the addition of barium nitrate. The pure crystals of the product were then collected, washed with alcohol and acetone, dried in a vacuum desiccator and then in an oven at 100°C for 3 hours. The yield was 40%.

Found: Co, 19.20%; PO_4, 31.50%; C, 23.81%; N, 18.37%; H, 6.81%.
Calculated for $Cotn_2PO_4$; Co, 19.50%; PO_4, 31.45%; C, 23.85%; N, 18.55%; H, 6.63%.

2.1.3 Phosphorus-32 labelled $Cotn_2PO_4$

The method described in Section 2.1.2 was used. 5mC of orthophosphate labelled with phosphorus-32 was injected into the mixture contained in a conical flask. Standard safety precautions for the handling of radioactive solutions were taken. Phosphorus-32 has a maximum β energy of 1.7 MeV and a half-life of 14.3 days. Difficulty was encountered in the removal of excess free phosphate from the complex. A saturated barium nitrate solution was used to test for the presence of free phosphate after each process of precipitation of free phosphate with ammonia as described before. The purity of the complex was finally assessed by making-up an aqueous solution and assaying for P^{32} in aliquor samples with and without separation in a Zeokarb 225 cation exchange column (Section 7.5.1 Chapter 7). This procedure gave an accurate measure of the percentage content of uncoordinated phosphate anion in the preparation.

2.1.4 Trans - Dichlorobis (ethylenediamine) cobalt (III) perchlorate

This complex was obtained by dissolving trans - $(Coen_2Cl_2)Cl$ [46] in water and re-precipitating with perchloric acid.

2.1.5 Phosphatobis (ethylenediamine) cobalt (III)

This complex was prepared by the method of Lincoln.[30]

2.1.6 Carbonato-bis (trimethylenediamine) cobalt (III) chloride

Low yields of product were obtained from preparations based on potassium triscarbonatocobaltate (III)[51] [52] probably due to potassium carbonate impurity.

2.1.7 Carbonato-bis (trimethylenediamine) cobalt (III) perchlorate

Sodium tris (carbonato) cobalt (III) complex was prepared according to the method of Bauer and Drinkard[47]. Olive green, $Na_3Co(CO_3)_3$. $3H_2O$ (10.8g.) was placed in an evaporating dish. Water (50ml.) was added and the mixture was heated on a steam bath with stirring. 100% trimethylenediamine (5ml.) was added. When the mixture had changed from green to dark red the dish was removed from the steam bath and allowed to cool. The solution was filtered to remove unreacted $Na_3Co(CO_3)_3 3H_2O$ and any cobalt oxide that might have formed. To the filtrate solid sodium perchlorate was added to make solution 8M in perchlorate and dark red crystals separated. The solution was kept in a refrigerator overnight and the crystals were collected and washed with alcohol. The complex was recrystallised by dissolving in the minimum amount of cold water and re-precipitating with sodium perchlorate. The recrystallised product was carefully washed with alcohol then with acetone and dried in a desiccator. The yield was 55%.

Found: C, 23.20% H, 5.65% N, 15.09% Cl, 9.85%

Calculated for $(Cotn_2CO_3)ClO_4$

C, 22.9% H, 5.50% N, 15.27% Cl, 9.70%.

2.1.8 Cis - Diaquo-bis (trimethylenediamine) cobalt (III) perchlorate [53]

To a weighed amount of carbonato-bis (trimethylenediamine) cobalt (III) complex, two equivalents of perchloric acid (4.13M) were added from a burette. Carbon dioxide gas was evolved during the process. After the completion of evolution of CO_2 the solution was left in a vacuum desiccator for a week. Crystals were obtained but because of their high solubility purification was difficult.

2.1.9 ATTEMPTS were made to isolate the trans - diaquo-bis (trimethylenediamine) cobalt (III) perchlorate adapting methods used by Bjerrum and Rasmussen,[48] Tong and Yankwich,[49] Kruse and Taube[50] to prepare analogous diaquo-bis (ethylenediamine) complexes but without success.

The problem with both the cis- and the trans- diaquo-bis (trimethylenediamine) complexes is their high solubility which makes their isolation difficult.

2.2 ANALYSIS

2.2.1 Cobalt - electrodeposition[54]

The complex $Cotn_2PO_4$ was converted to cobalt sulphate by the following method. $Cotn_2PO_4$ (0.28g.) was dissolved in concentrated A.R. sulphuric acid (8ml.) and concentrated A.R. nitric acid (2ml.). A.R. sodium sulphate (approx. 1g.) was added and the solution was heated on a hotplate until brown fumes of nitrogen dioxide was evolved. A.R. nitric acid was further added dropwise to fume away the organic residue. This was repeated 5 to 6 times. The solution was then cooled and added slowly to a solution of A.R. ammonium sulphate (4g.) and hydrazine sulphate (approx. 1g.) in 70ml. water. 0.88 ammonia (40ml.) was then added and the solution was electrolysed using a current of 3 amps for 1½ hours. The reproducibility of the analysis was within 1%.

2.2.2 Phosphate - pH titration

A 25ml. mixture of 0.0269M complex (5ml.), 0.0236M $HClO_4$ (10ml.) and 0.4M $NaClO_4$ (10ml.) was titrated with standardised 0.104M NaOH using the Radiometer pH meter 25, Titrator II. All solutions were made up with CO_2- free water.

2.2.3 Carbon, nitrogen, hydrogen, chlorine-microanalysis

The analyses of these elements were performed by the C.S.I.R.O Microanalytical Service, Melbourne.

CHAPTER 3

STRUCTURAL INVESTIGATION AND EQUILIBRIA OF BIS(TRIMETHYLENEDIAMINE) COBALT (III) - PHOSPHATE SYSTEM

3.1 Evidence for Coordination of Phosphate

The $(Co(NH_3)_4PO_4)^0$ and $(Co(en)_2PO_4)^0$ species have been isolated and confirmed to have the phosphate ligand coordinated in the bidentate form[31]. The corresponding monodentate phosphato species, $(Co(NH_3)_4OH_2.HPO_4)^+$ and $(Co(en)_2OH_2.HPO_4)^+$ have also been prepared as the nitrate and perchlorate salts respectively. These conclusions for the coordination of the phosphate ligand to the cobalt (III) centre have been drawn from infra-red spectral evidence combined with additional evidence from UV-visible spectra, P.M.R. spectra and measured acidity constants of the respective phosphato complexes.

It was further shown that the phosphato ligand was genuinely coordinated to a cobalt (III) centre by the slow rate at which the phosphato ligand is substituted by other ligands. Moreover, an equilibrium between free and coordinated P^{32} labelled phosphate was demonstrated after hydrolysis equilibrium has been established.

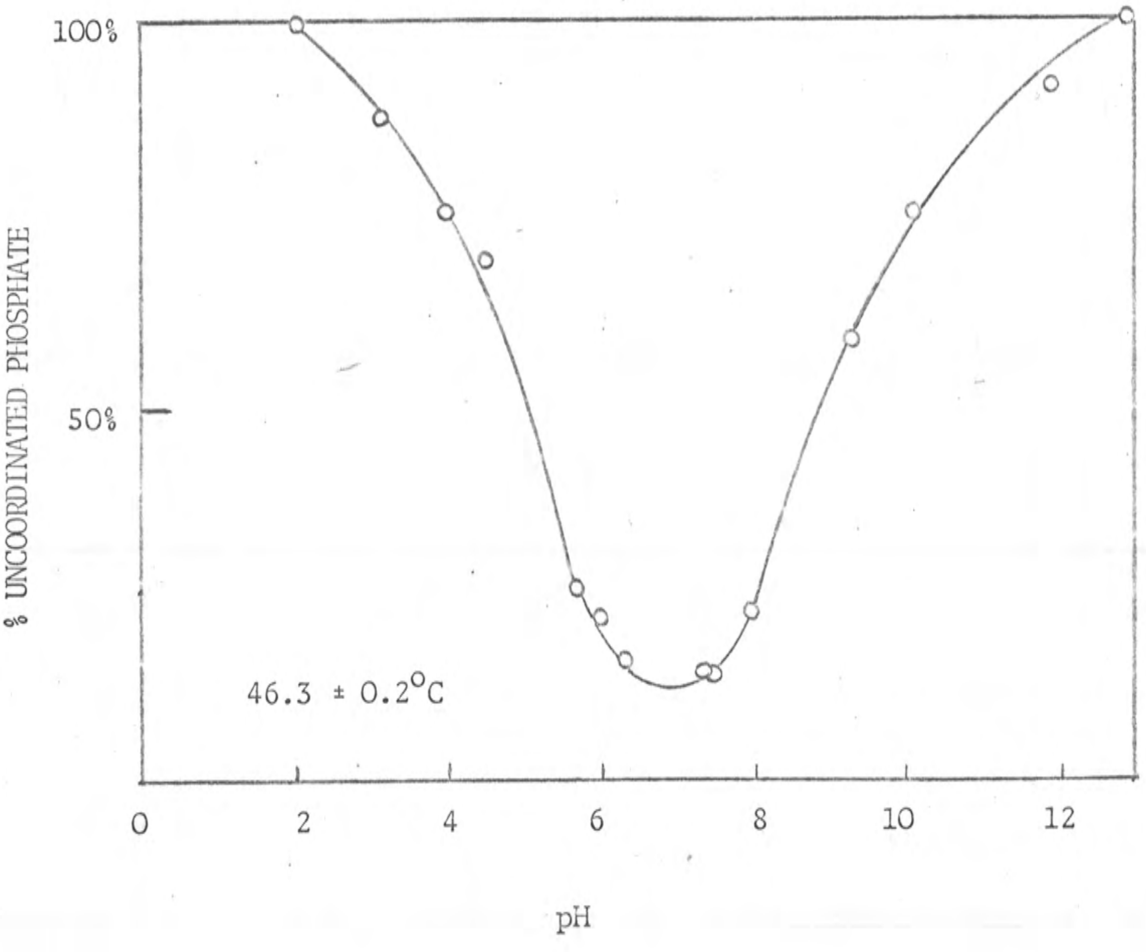
3.2 Equilibrium between Coordinated and Non-coordinated Phosphate in the bis(trimethylenediamine) cobalt (III) system

Solutions of $Cotn_2P^{32}O_4$ at various pH's in the range of 2 to 13 were equilibrated at 46.3°C. The percentage of uncoordinated phosphate was determined by separating and counting the free phosphate released as described in Section 7.5.1, Chapter 7. In Fig. 3.1 the

FIG. 3.1

EQUILIBRIUM PROFILE FOR

BIS(TRIMETHYLENEDIAMINE) COBALT (III) SYSTEM



variation of the percentage uncoordinated phosphate with pH is shown. It is found that maximum coordination occurs in the narrow pH range of 5.5 to 8.5. Below pH 2 and above pH 13, the degree of coordination is essentially zero.

3.3 Infra Red Spectra and Structural Assignments

Studies of alkali-metal orthophosphates show that the tetrahedral orthophosphate anion, with Td symmetry, exhibits four fundamental frequencies,[55-57] namely 970-980cm^{-1} (ν_1), 363-388cm^{-1} (ν_2), 1080-1082cm^{-1} (ν_3) and 500-515cm^{-1} (ν_4). The fundamental frequencies ν_1 and ν_2 are infra-red inactive but are Raman active.

The 800-1200cm^{-1} range, involving the ν_1 and ν_3 fundamentals, is of considerable interest for the determination of the symmetry of the coordinated phosphato ligand. Coordination of a phosphate ligand to a metal ion is usually accompanied by

(1) the appearance of new bands and splitting of degenerate modes due to lowering of symmetry,

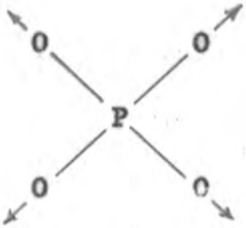
(2) frequency shifts of bands,

(3) intensification of spectra.

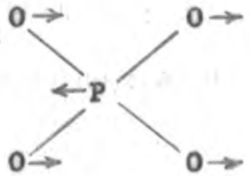
The symmetry of a monodentate phosphato ligand should be C_{3v}. This lowering of symmetry from Td to C_{3v} should make the ν_1 frequency infra-red active with medium intensity and split the degenerate ν_3 fundamental into two intense, sharp bands. This is found to be so in the infra-red spectra of $Co(NH_3)_5PO_4{}^0$, and $(Co(NH_3)_4(H_2O)HPO_4)^+$.[31]

A bidentate phosphato ligand should exhibit C_{2v} symmetry. The original ν_3 fundamental should split into three bands. The assignments of the ν_1 and ν_3 fundamentals in $Coen_2PO_4{}^0$ and $Co(NH_3)_4PO_4{}^0$ [31] favour a bidentate phosphato ligand. The splitting of bands predicted by Group Theory is given in Table 3.1.

The ν_1 and ν_3 fundamentals arise from the symmetrical and unsymmetrical stretching of the phosphate group.



ν_1 (symmetrical)



ν_3 (unsymmetrical)

The infra-red spectrum of the $(Cotn_2PO_4)^0$ complex shown in Fig. 3.2 exhibits four bands due to the phosphato ligand in the 800-1200cm^{-1} range. These are assigned as follows:
895cm^{-1} (ms) ν_3, 915cm^{-1} (m) ν_1, 1045cm^{-1} (vs) ν_3, and 1102cm^{-1} (s) ν_3.

The absorptions at 975cm^{-1}, 1145cm^{-1} and 1180cm^{-1} have been attributed to the trimethylenediamine groups and are assigned as shown in Table 3.2 by comparison with infra-red spectra of $(Cotn_3)Cl_3$, $(Cotn_3)I_3$ and $(Coen_2PO_4)$.

Table 3.1

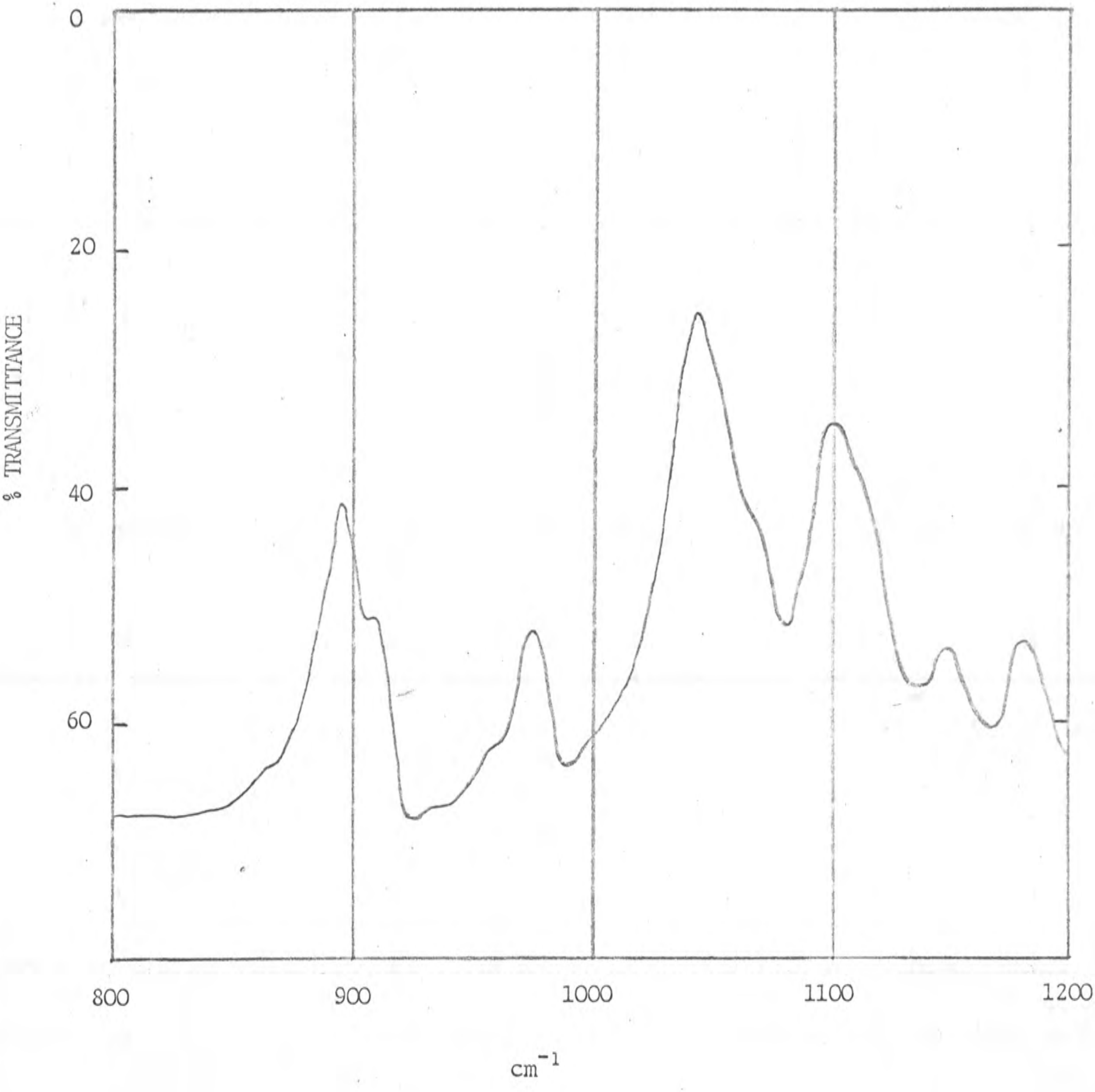
Correlation between Td, C_{3v} and C_{2v}.

	ν_1	ν_2	ν_3	ν_4
Td	A_1(R)	E(R)	F_2(I,R)	F_2(I,R)
C_{3v}	A_1(I,R)	E(I,R)	A_1(I,R) + E(I,R)	A_1(I,R) + E(I,R)
C_{2v}	A_1(I,R)	A_1(I,R) + A_2(R)	A_1(I,R) + B_1(I,R) + B_2(I,R)	A_1(I,R) + B_1(I,R) + B_2(I,R)

I = infra-red active R = Raman active

FIG. 3.2

INFRA-RED SPECTRUM OF $(Co(tn)_2PO_4)^0$



Lincoln and Stranks[31] reported infra-red absorption bands for $(Co(NH_3)_4PO_4)^0$ and $(Coen_2PO_4)^0$ in the same range and have assigned these to the phosphato ligand as follows:

$(Co(NH_3)_4PO_4)^0$

900cm^{-1} (m) ν_1, 920cm^{-1} (s) ν_3, 1045cm^{-1} (s) ν_3 and 1110cm^{-1} (s) ν_3

$(Coen_2PO_4)^0$

900cm^{-1} (ms) ν_3, 915cm^{-1} (m) ν_1, 1050cm^{-1} (vs) ν_3 and 1085cm^{-1} (s) ν_3.

The fundamental frequencies assigned for ν_1 and ν_3 in $(Cotn_2PO_4)^0$ are very close to those assigned to $(Co(NH_3)_4PO_4)^0$ and $(Coen_2PO_4)^0$. Hence the infra-red evidence confirms a bidentate phosphato ligand in the $(Cotn_2PO_4)^0$ complex.

Table 3.2

Infra-red spectrum of $Cotn_2PO_4$

Absorption Max. (cm^{-1})	Assignment
895 (ms)	ν_3
915 (m)	ν_1
975 (m)	N-H
1045 (vs)	ν_3
1102 (s)	ν_3
1145 (m)	N-H
1180 (m)	C-H

3.4 Stereochemical Configuration of $(Cotn_2(OH_2)H_2PO_4)^{2+}$

3.4.1 UV-visible Solution Absorption Spectra

An aqueous solution of $(Cotn_2PO_4)^0$ exhibits an UV-visible spectrum with maxima at 374mμ (ε = 99) and 540mμ (ε = 105), as shown in Fig. 3.3 (Curve A). On acidification to about pH 2, where it will be shown below that the cis- $(Cotn_2(OH_2)H_2PO_4)^{2+}$ species predominates, the spectrum rapidly shifts to shorter wavelength maxima, accompanied by a fall in extinction coefficients at 367mμ (ε = 74) and 520mμ (ε = 67) (Curve B). It is found that on readjustment of the pH to about 6, the spectral changes are reversed. On adjustment of the pH to about 11, where the cis- $(Cotn_2(OH)PO_4)^{-1}$ species is predominant, the maxima appear at 374mμ (ε = 103) and 538mμ (ε = 103) (Curve C).

The shift to shorter wavelengths on acidification is consistent with the replacement of the phosphato ligand by one aquoligand having a larger ligand field splitting than the phosphato ligand. The similar spectral characteristics of the monodentate phosphato species, the bidentate phosphato species and cis- $(Cotn_2(OH_2)_2)^{3+}$ (Fig. 6.1 Chapter 6) suggest that $(Cotn_2(OH_2)H_2PO_4)^{2+}$ would have a cis- configuration. Trans- $(Co(en)_2(H_2O)_2)^{3+}$ has shown to exhibit three absorption maxima at 550, 435 and 340mμ [48] and a similar spectrum should arise from a trans- aquophosphato complex.

FIG. 3.3

UV-VISIBLE SOLUTION ABSORPTION SPECTRA OF PHOSPHATO-BIS(TRIMETHYLENEDIAMINE) COBALT (III) COMPLEX IONS

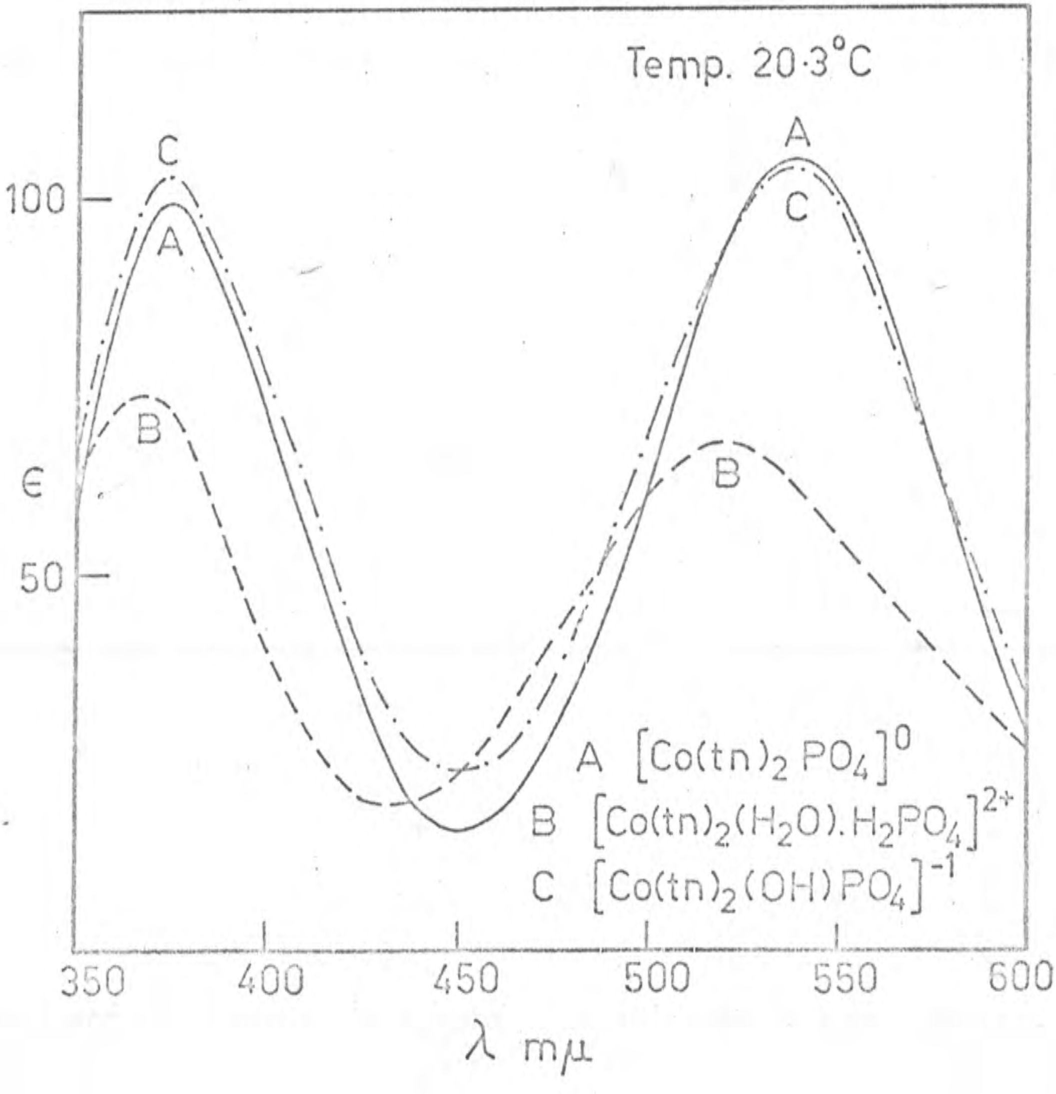


Table 3.3

Solution Absorption Maxima of Phosphato Complexes

Complex	Maxima	
$Coen_2PO_4$ ^{0}	377mμ (ε = 97.9)	529mμ (ε = 112.0)
$Cotn_2PO_4$ ^{0}	374mμ (ε = 99)	540mμ (ε = 105)
$(Coen_2(H_2O)HPO_4)^+$	366mμ (ε = 53.8)	511mμ (ε = 107.6)
$(Cotn_2(H_2O)H_2PO_4)^{2+}$	367mμ (ε = 74)	520mμ (ε = 67)

3.4.2 Proton Magnetic Resonance Spectrum

Proton magnetic resonance spectroscopy enables cis- and trans- isomers of $(Coen_2X_2)$ complexes to be distinguished[58]. The PMR spectra of the enCo (III) species depends on the environment of the protons of the en ligand which in turn depends on the symmetry of the Co (III) species.

The main requirements for PMR study are:

(1) Sufficiently high solubility (⩾ 0.3M) of the Co (III) species in the solvent employed.

(2) Slow exchange of the amino protons with solvent.

(3) Stability of the Co (III) species in the solvent used.

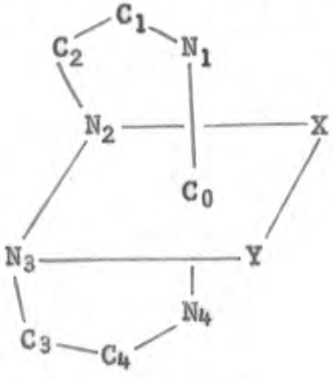
Jolly, Harris and Briggs[59] found certain advantages in using concentrated sulphuric acid as a solvent for the PMR studies of cobalt ammine complexes namely:

(1) Most of complexes are soluble in sulphuric acid to the extent of at least 1M compared to their solubilities in water which are generally less than 0.2M.

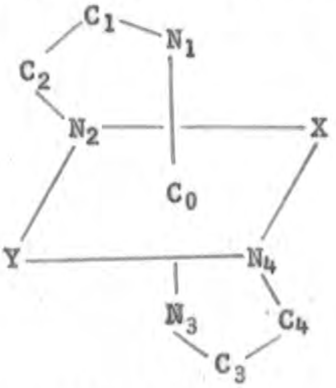
(2) The H_2SO_4 solvent peak is far removed from the ammine peaks which enables the undeuterated solvent to be used.

(3) Exchange rates between protons of the ligand and that of solvent are slow.

In *trans*- (Coen$_2$XY), all N-atoms are in similar environments. Therefore only a single N-H absorption peak would be expected.



cis- isomer



trans- isomer

All the 4 C-atoms are in similar environments but splitting may occur due to the following two factors:

(1) Slight differences in the relatives effects experienced by C_2 and C_3 compared to C_1 and C_4 due to X and Y.

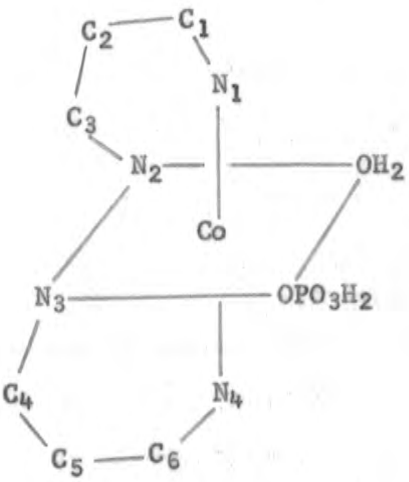
(2) The possible existence of the en ligand in the envelope and gauche conformations (splitting will be observed if the interconversion of these two conformers is slow).

In the case of the *cis*- isomer, N-H absorption peaks can arise due to the following environments.

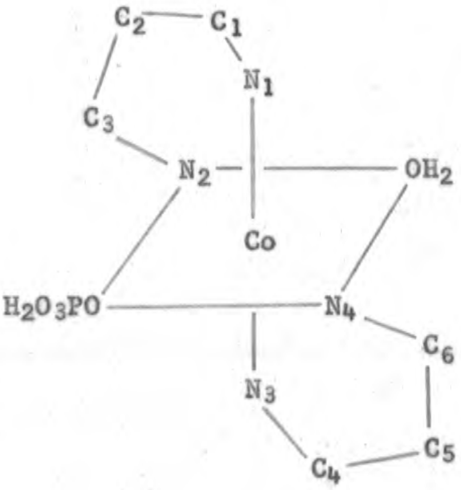
N_1 *cis* to X, *cis* to Y; N_4 *cis* to X, *cis* to Y
N_2 *cis* to X, *trans* to Y
N_3 *cis* to Y, *trans* to X

Two CH- absorption peaks will be observed if conformer interconversion is fast, otherwise, four peaks may be observed.

These predictions can be extended to the ($Cotn_2XY$) case, where the amine ring is six-membered instead of five-membered. The predicted number of N-H absorptions in the *cis*- and the *trans*- isomers should be the same as for the en complex.



cis- isomer

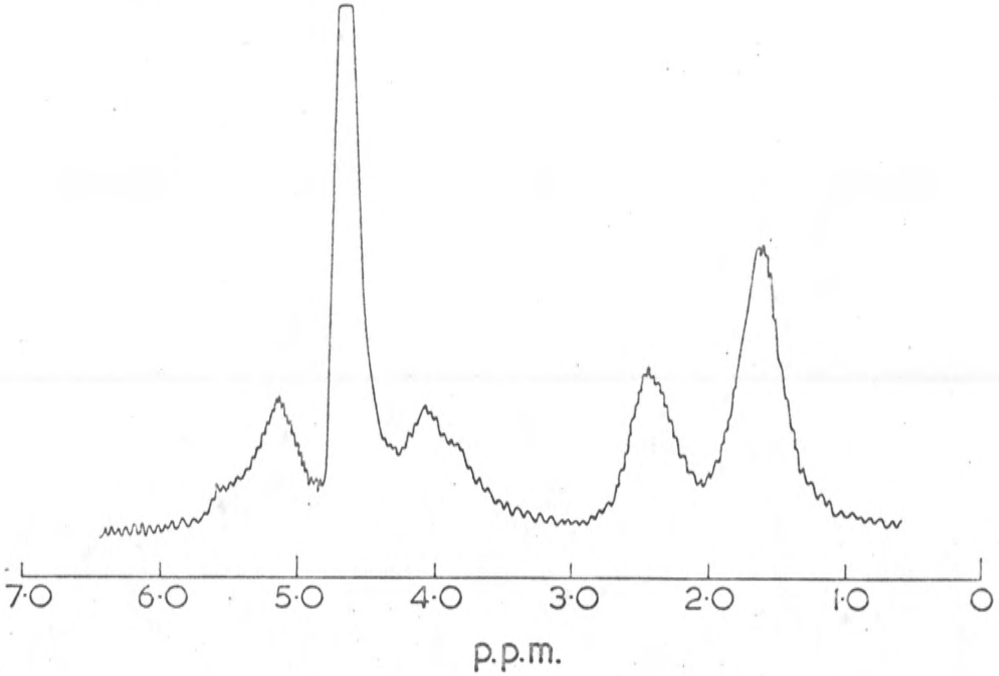


trans- isomer

Fig. 3.4 shows the PMR spectrum of the $(Cotn_2(H_2O)H_2PO_4)^{2+}$ species in 0.25M H_2SO_4/99.9% D_2O at 2°C.

FIG. 3:4

PMR SPECTRUM OF cis-$[Co\,tn_2\,H_2O\,H_2PO_4]^{2+}$ IN 0·25M H_2SO_4/99·9 % D_2O at 2°C.



Two NH peaks appear at 5.1_2 and 4.0_3 p.p.m. (relative to trimethylsilane (TMS) external standard) with an intensity ratio of 4:4 which are interpreted to arise respectively from

(1) N_1 cis to H_2O, cis to OPO_3H_2; N_4 cis to H_2O cis to OPO_3H_2

(2) N_2 cis to H_2O, trans to OPO_3H_2; N_3 trans to H_2O cis to OPO_3H_2

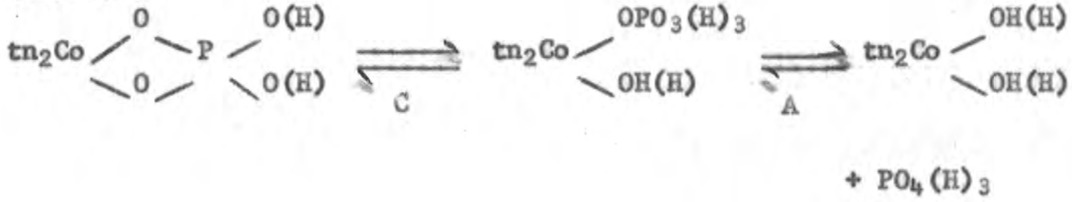
The peak at 4.0_3 p.p.m should comprise of two amine-hydrogen peaks for cis H_2O, trans H_2PO_4 and trans H_2O, cis H_2PO_4 with an intensity ratio of 2:2. The virtual coincidence of these two peaks is also observed in the PMR spectrum of $(Coen_2(OH_2)HPO_4)^+$ measured with 60Mc frequency[31]. Measurements at 100Mc frequency may, however, have better peak resolution. The peaks are separately by 64.8 c/s compared to the corresponding NH_2 shifts for the $(Co(en)_2OH_2.OPO_3H_2)^{2+}$ of 94.4 c/s. There is hence a substantial reduction in the chemical shifts from the en complex to the tn complex. The two C-H absorption peaks at 2.4_0 and 1.8_9 p.p.m. are in an intensity ratio of 4:8. These are interpreted to be due to C_2 and C_5; and C_1, C_3, C_4 and C_6 respectively. No resolution of possible conformations of CH- groups was observed at 60Mc/s.

All this evidence clearly indicates that $(Cotn_2(H_2O)H_2PO_4)^{2+}$ exists as the cis- isomer.

3.5 The acidity constants for the monodentate and bidentate phosphato complex ions

Spectral and P^{32}- hydrolysis studies, show that the following equilibria are ultimately established in aqueous solutions of the complex (Chapters 4 and 5).

(E.3.1)



The chelation equilibrium, C, is established much more rapidly than the hydrolysis anation equilibrium, A. (H) is used in the general equation to indicate the possible degrees of protonation of the ligands in aqueous media.

The bidentate species $(Cotn_2PO_4)^0$ may be titrated with perchloric acid at 5^oC. One distinct end point may be recognised and assigned to the proton equilibrium

$$Cotn_2PO_4H^+ \; + \; aq \rightleftharpoons Cotn_2PO_4{}^0 \; + \; H^+_{aq} \quad Ka_1$$

In a medium of 0.16M sodium perchlorate, a value for pKa_1 of 4.12 ± 0.05 is obtained at 5^oC.

To obtain the monodentate species, two mole-equivalents of perchloric acid was added to a solution of bidentate to open the chelate ring. This occurs rapidly at room temperature. The resulting solution of the dihydrogen monodentate species $(Cotn_2(OH_2)PO_4H_2)^{2+}$ was then back titrated with sodium hydroxide. Three distinct end points were recognised and assigned to the protonic equilibria.

(E.3.2)

$$(\mathrm{Cotn_2(OH_2)PO_4H_2})^{2+} + \mathrm{aq} \rightleftharpoons (\mathrm{Cotn_2(OH_2)PO_4H})^{+} + \mathrm{H^{+}aq} \quad \mathrm{Ka_2}$$

(E.3.3)

$$(\mathrm{Cotn_2(OH_2)\ PO_4H\ })^{+} + \mathrm{aq} \rightleftharpoons (\mathrm{Cotn_2(OH)PO_4H})^{0} + \mathrm{H^{+}aq} \quad \mathrm{Ka_{aq}}$$

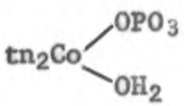
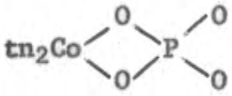
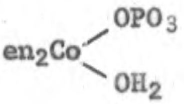
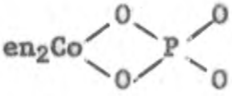
(E.3.4)

$$(\mathrm{Cotn_2(OH)PO_4H})^{0} + \mathrm{aq} \rightleftharpoons (\mathrm{Cotn_2(OH)PO_4})^{-} + \mathrm{H^{+}aq} \quad \mathrm{Ka_1}$$

$\mathrm{Ka_{aq}}$ describes the equilibrium involving the aquoligand acting as a proton donor while $\mathrm{Ka_2}$ and $\mathrm{Ka_1}$ refer to the equilibrium wherein the di- and mono- protonated phosphato ligands function as proton donors.

Table 3.4

pKa values

Complex Ion	Temp °C	pKa_{aq}	pKa_1	pKa_2
 $tn_2Co(OPO_3)(OH_2)$	5[a]	6.07±0.05	10.74±0.05	2.66±0.05
	20.3[a]	5.18±0.05	10.62±0.05	2.98±0.05
			(ΔH = 4.8)	
	5[a]		4.12±0.05	
 $en_2Co(OPO_3)(OH_2)$	5[b]	7.25±0.05	9.75±0.05	3.30±0.05
	23.0[b]	6.75±0.05	9.40±0.05	3.10±0.05
		(ΔH=8.8±0.4)	(ΔH = 7.7±0.5)	(ΔH = 3.7±0.4)
	5[b]		4.25±0.05	
H_3PO_4	19.7[c]		12.5	5.922

a = This work (μ = 0.16)

b = Lincoln and Stranks (μ = 1)

c = Schmidt and Taube (μ = 1)

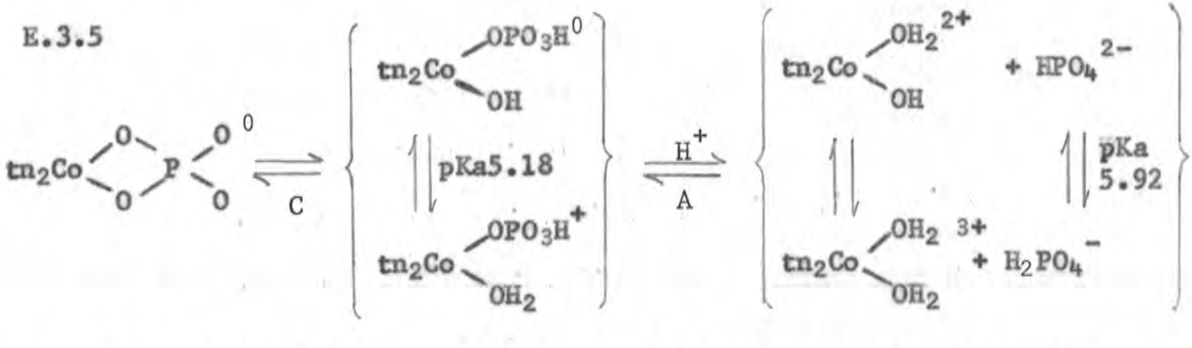
ΔH in $kcal.mole^{-1}$

3.6 Discussion

It has been shown by the study of the hydrolysis equilibrium and spectral studies that the phosphato ligand may be coordinated in a significant proportion to the cobalt (III) only within the pH range of 5.5 and 8.5. In the preparation of the phosphato bis (trimethylenediamine) cobalt (III) complex it was found that adjustment of the pH of the reaction mixture to about pH 8 was necessary for the precipitation of the complex. Once precipitation commences, the equilibrium is continuously shifted towards the coordinated phosphate side. Below pH 5 highly soluble protonated phosphato complexes are formed which undergo complete hydrolysis via aquophosphato complexes. Above pH 9, base hydrolysis of the phosphato ligand occurs. Hence for successful isolation of crystalline bidentate phosphato complexes, it is necessary to know these equilibrium and hydrolytic properties.

Within the pH range 5.5 to 8.5, the predominant bis-(trimethylenediamine) species are inter-related by two successive equilibria and corresponding protonic equilibria.

E.3.5



where C is the chelation equilibrium and A is the hydrolysis anation equilibrium. The values of pKa quoted are those for the cis-isomers at 20.3°C in 0.16M $NaClO_4$. The degree of coordination of phosphate in this system depends critically on the position of the chelation equilibrium, C. This equilibrium, which involves opposing ring-opening and ring-closing reactions, is established within minutes at room temperature while the hydrolysis-anation equilibrium, A, is established in several hours. Outside the pH range of 5.5 to 8.5, the bidentate rapidly and completely transforms to the monodentate complexes which ultimately undergo complete hydrolysis.

Coordination of the phosphato ligand to the cobalt (III) increases its acidity compared to the free orthophosphate anion. The anion $HPO_4{}^{2-}$ has a pKa value of 12.5, but on coordination as the $-OPO_3H$ ligand, the pKa value becomes 10.62. On further coordination as a bidentate ligand, the pKa decreases to a value of 4.00 with a marked enhancement of its acidity. For the $H_2PO_4{}^{-}$ anion this was also observed to be the case. The pKa value decreases from 5.92 to 2.98 on coordination as a monodentate ligand which further decreases to a pKa value of -0.44 on coordination as a bidentate ligand (Section 4.4, Chapter 4).

Coordination of the phosphate to a positive cobalt (III) centre may also be regarded to be equivalent to the attachment of a proton. If this alternative interpretation is considered, then the pKa value of $-OPO_3H$ should be compared to the pKa value of

$H_2PO_4^-$. As such, the basicity of phosphate is greater when it is bonded to cobalt (III) than when it is bonded to hydrogen (I) which is consistent with the mixed σ-π character of Co-OPO_3 bond.

In addition, it is observed that replacement of the ethylenediamine groups by the trimethylenediamine groups appears to have enhanced the acidity of the aquo ligand by $\Delta pK = +1.18$ at 5°C. Lincoln and Stranks[31] found that replacement of the two ethylenediamine groups by four amine groups enhances the acidity of the aquo ligand by $\Delta pK = +0.45$.

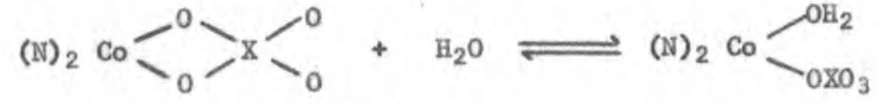
CHAPTER 4

RING OPENING REACTIONS OF PHOSPHATO-COBALT (III) SYSTEMS

4.1 Introduction

Lincoln and Stranks[31] have shown that an equilibrium can exist between monodentate and bidentate oxyanions cobalt (III) species in aqueous solution. For an XO_4 ligand, an equilibrium of this kind is shown below.

E.4.1

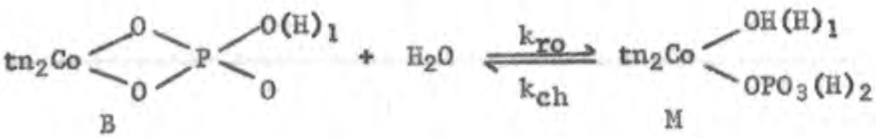


where N is a non-reacting ligand. They have studied the rates of ring opening and chelation of the phosphato bis(ethylenediamine) cobalt (III) system in aqueous media at a single temperature (22.5°).

4.2 Ring opening of $Cotn_2PO_4$ in pH range 3 to 5

The equilibrium that exists between the bidentate and monodentate phosphato ligands in the bis(trimethylenediamine) cobalt (III) system may be represented by the general equation

E.4.2



where k_{ro} is the rate constant for the opening of the phosphato chelate ring, k_{ch} is the rate constant for the formation of the phosphato chelate ring and $(H)_n$ indicates the possible degrees of protonation.

The approach to equilibrium from the bidentate side was followed spectrophotometrically, the experimental details of which are given in Section 7.3.2 Chapter 7. Good first order plots were obtained and some typical rate plots are shown in Fig. 4.1. Infinite time readings were taken after at least eight reaction half-times.

Since the reaction is reversible, the observed rate comprises contributions from the forward and backward reactions, hence

E.4.3 $$k_{obs} = k_{ro} + k_{ch}$$

The equilibrium constant, K_{eq}, was calculated from the measured optical density of the equilibrated solution and the known extinction coefficients of the monodentate (M) and bidentate (B) complexes. Since at equilibrium

E.4.4 $$k_{ro}\ (B)_{eq} = k_{ch}\ (M)_{eq}$$

Then

E.4.5 $$K_{eq} = \frac{k_{ro}}{k_{ch}} = \frac{(M)_{eq}}{(B)_{eq}}$$

Using equations (E.4.4) and (E.4.5), the rate constants, k_{ro} and k_{ch}, can be calculated for the reaction at each pH. These values are tabulated in Table 4.1.

Fig. 4.2 shows the percentage bidentate-monodentate equilibrium plotted against pH. The derived values of k_{ro} and k_{ch} are also plotted. It can be seen that above pH 5, the bidentate phosphato species predominates. The values of k_{ro} are seen to increase rapidly as the pH decreases from pH 3.5.

FIG. 4.1

TYPICAL FIRST ORDER RATE PLOTS

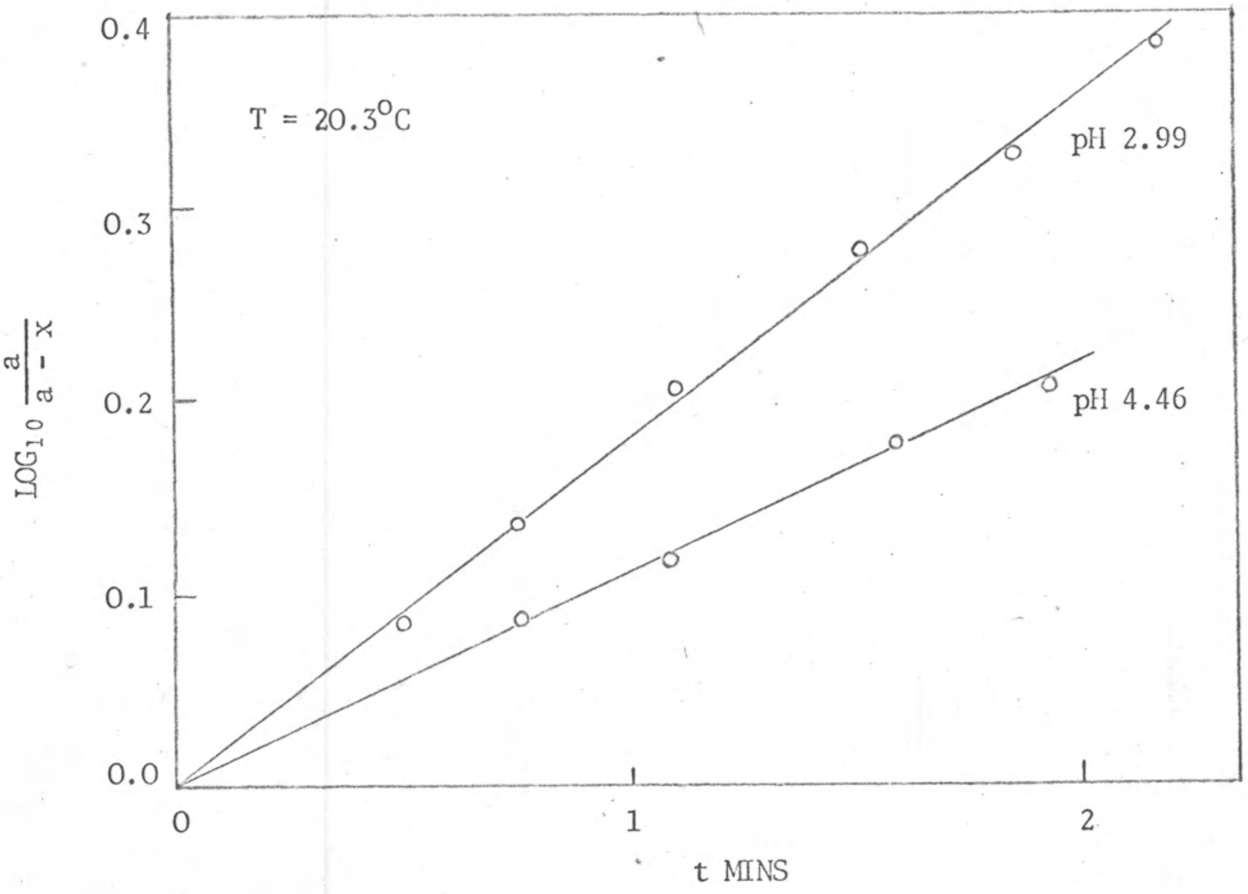
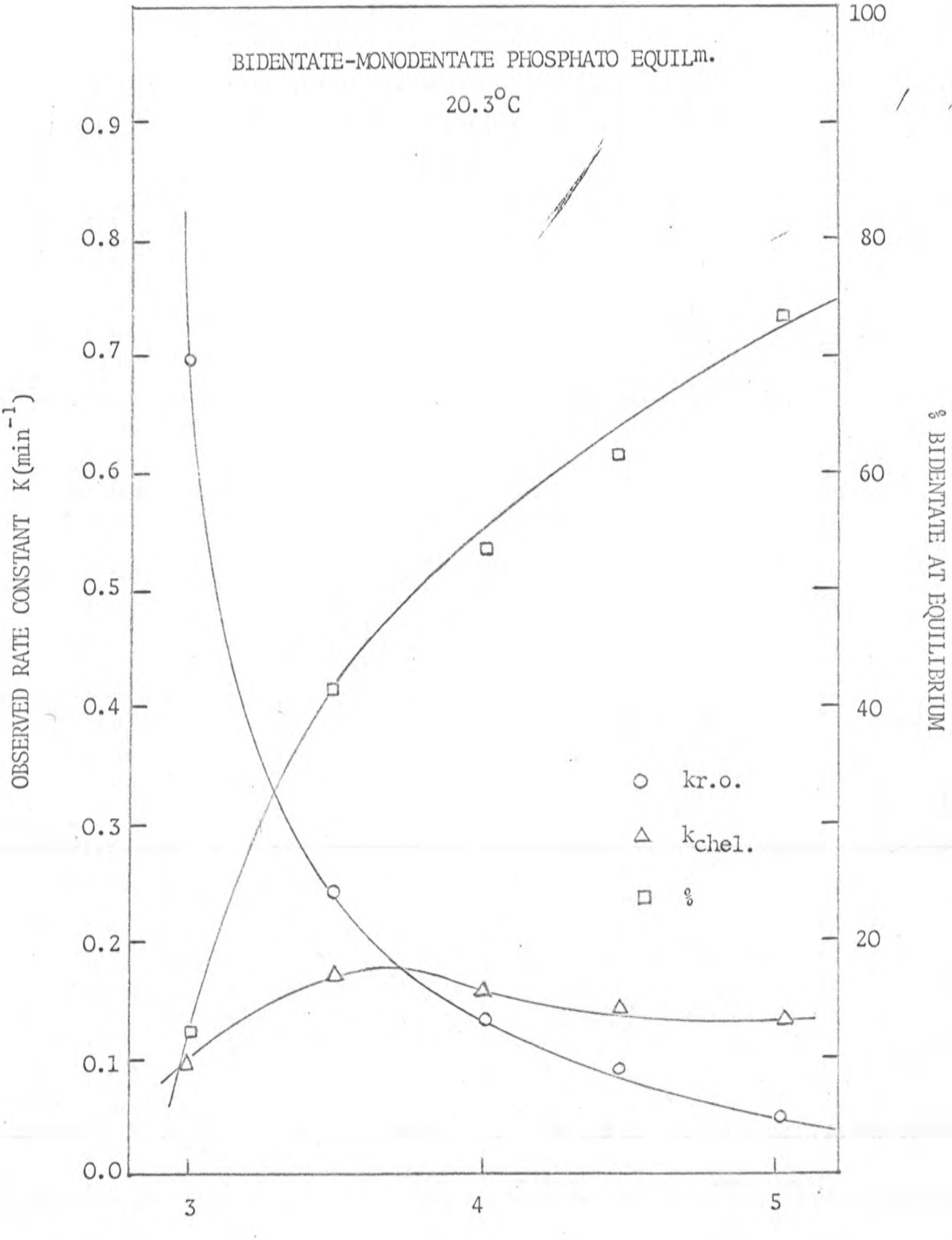


FIG. 4.2



BIDENTATE-MONODENTATE PHOSPHATO EQUIL^{m}.
20.3^{o}C
OBSERVED RATE CONSTANT K(min^{-1})
% BIDENTATE AT EQUILIBRIUM
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
100
80
60
40
20
3
4
5
○ kr.o.
△ $k_{chel.}$
□ %

Table 4.1

Rates of Ring Opening and Chelation at 20.3°C

pH	$k_{ro} \times 10$ (min^{-1})	f_o	$k_{ch} \times 10$ (min^{-1})	% bidentate at equilibrium
5.02	0.5 ± 0.2	0.087	1.3 ± 0.1	73.8
4.46	0.9 ± 0.2	0.258	1.4 ± 0.1	61.5
4.00	1.3 ± 0.3	0.50	1.5 ± 0.1	53.9
3.49	2.4 ± 0.3	0.764	1.7 ± 0.1	41.7
2.99	7.2 ± 0.6	0.91	0.99 ± 0.07	12.2

f_o = fraction of protonated bidentate

In the pH range 3 to 5, the rate law for the rate of opening of the phosphato ring, R_{ro}, can be written

$$\text{E.4.6} \qquad R_{ro} = k_{ro}(\text{Cotn}_2\text{PO}_4{}^0 + \text{Cotn}_2\text{PO}_4\text{H}^+)$$

$$= k_{ro}{}^{o}(\text{Cotn}_2\text{PO}_4{}^0) + k_{ro}{}^{H}(\text{Cotn}_2\text{PO}_4\text{H}^+)$$

Hence,

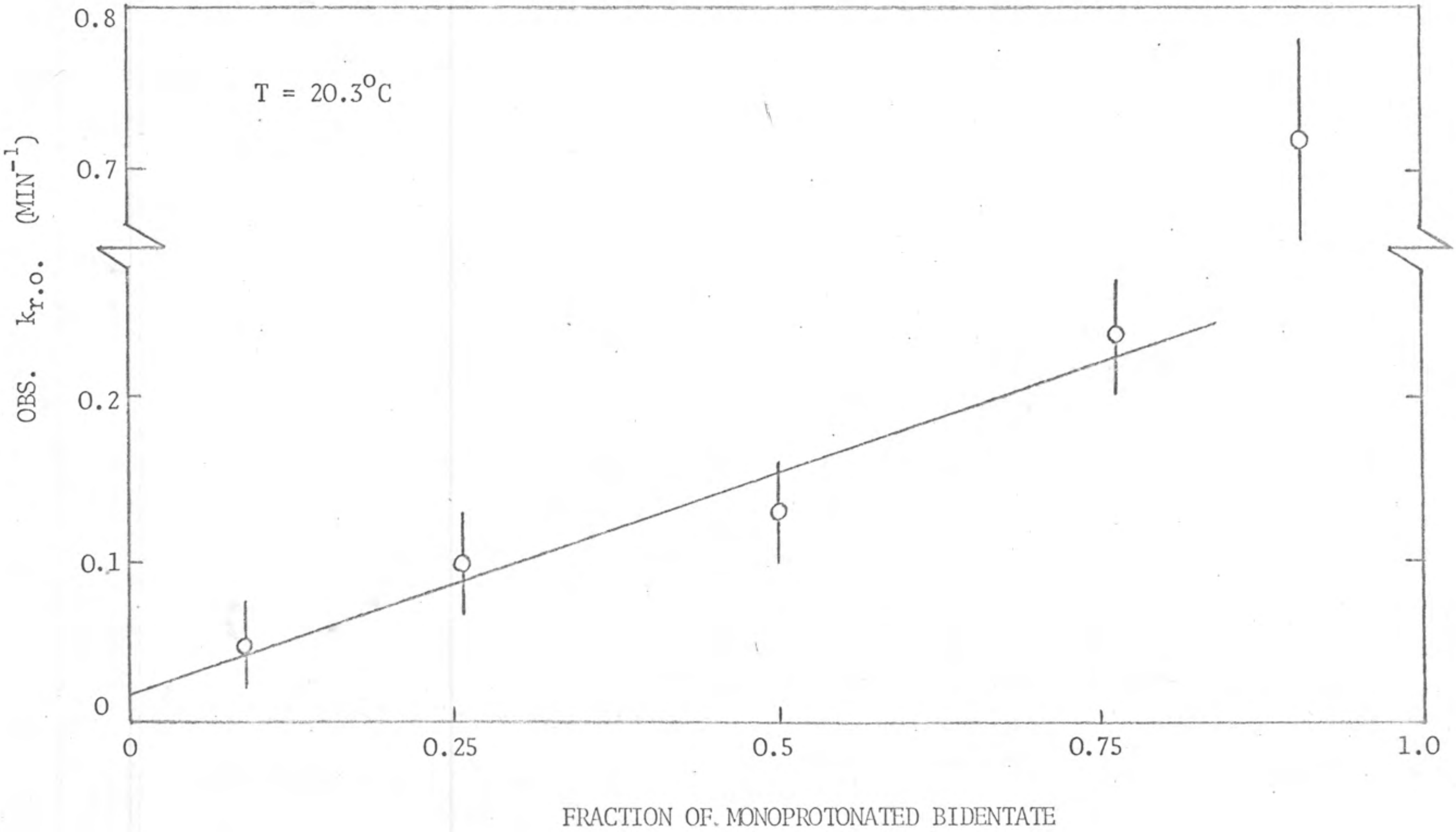
$$\text{E.4.7} \qquad k_{ro} = k_{ro}{}^{o} f_o + k_{ro}{}^{H^+} f_H$$

where f_o is the fraction of the unprotonated bidentate complex and f_H is the fraction of the monoprotonated bidentate complex.

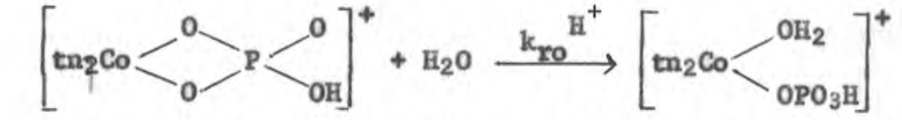
Assuming the same enthalpy of ionisation, ΔH, of 4.8 kcal. mole^{-1} as for the monodentate complex, a pK_a value of 4.00 is

FIG. 4.3

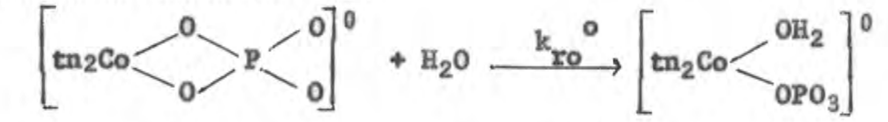
BIDENTATE → MONODENTATE



calculated for the bidentate at 20.3°C from the pK_a value determined at 5°C. The rate constant, k_{ro}, for ring opening can then be plotted against the fraction of monoprotonated bidentate as shown in Fig. 4.3. This can be seen to give a linear relationship. From the slope a value of 0.29 ± 0.02 min^{-1} was obtained for $k_{ro}^{H^+}$ which refers to the reaction

E.4.8 

A value of $(1.8 \pm 0.5) \times 10^{-1}$ min^{-1} was obtained from the intercept for k_{ro}^{o}, which indicates that

E.4.9 

in the pH range 3 to 5, the acid catalysed term, denoted by the rate constant, $k_{ro}^{H^+}$, predominates.

4.3 Chelation in the pH range 3 to 5

Depending on the pH of the aqueous media, the chelation reaction can involve any of the following three species: $(Cotn_2(OH_2)OPO_3H_2)^{2+}$ (P2), $(Cotn_2(OH_2)OPO_3H)^{+}$ (P1) and $(Cotn_2(OH)OPO_3H)^{0}$ (P0). The general rate law for chelation of the monodentate phosphato species may be written:

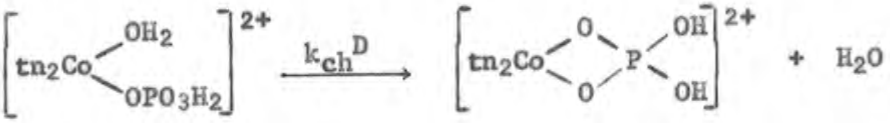
E.4.10

$$\text{Rate} = k_{ch}\ (\text{total monodentate phosphato species})$$

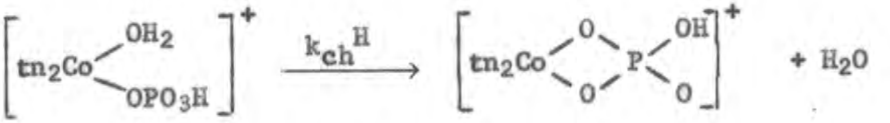
$$= k_{ch}^{D}\ (\text{Cotn}_2(\text{OH}_2)\text{OPO}_3\text{H}_2{}^{2+}) + k_{ch}^{H}\ (\text{Cotn}_2(\text{OH}_2)\text{OPO}_3\text{H}^{+}) + k_{ch}^{o}\ (\text{Cotn}_2(\text{OH})\text{OPO}_3\text{H}^{0})$$

where k_{ch} is the observed rate constant for the overall chelation reaction and k_{ch}^{D}, k_{ch}^{H}, k_{ch}^{o} are the specific first order rate constants defined by the following equations

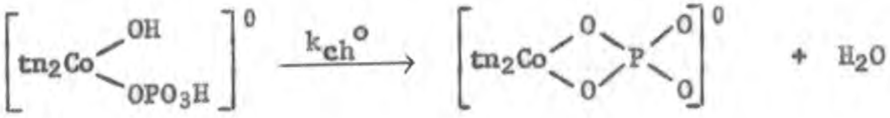
E.4.11



E.4.12



E.4.13



Knowing the total concentration of the monodentate species, and the acidity constants pK_{a_2} (2.98) and $pK_{a_{aq}}$ (5.18), the fractions of each monodentate species present at the various pH's can be calculated. The rate constants k_{ch}^{D}, k_{ch}^{H} and k_{ch}^{o} can be determined by solving equation of the form

E.4.14 $$k_{ch} = k_{ch}^{D} f_2 + k_{ch}^{H} f_1 + k_{ch}^{o} f_0$$

Table 4.2

Chelation Data at 20.3°C

pH	$k_{ch} \times 10$ (min^{-1})	f_0	f_1	f_2
5.02	1.3 ± 0.1	0.407	0.588	0.005
4.46	1.4 ± 0.1	0.157	0.808	0.035
4.00	1.5 ± 0.1	0.056	0.853	0.091
3.49	1.7 ± 0.1	0.015	0.749	0.236
2.99	0.99 ± 0.07	0.002	0.522	0.475

f_o = fraction of $(Cotn_2(OH)PO_4H)^0$

f_1 = fraction of $(Cotn_2(OH_2)PO_4H)^+$

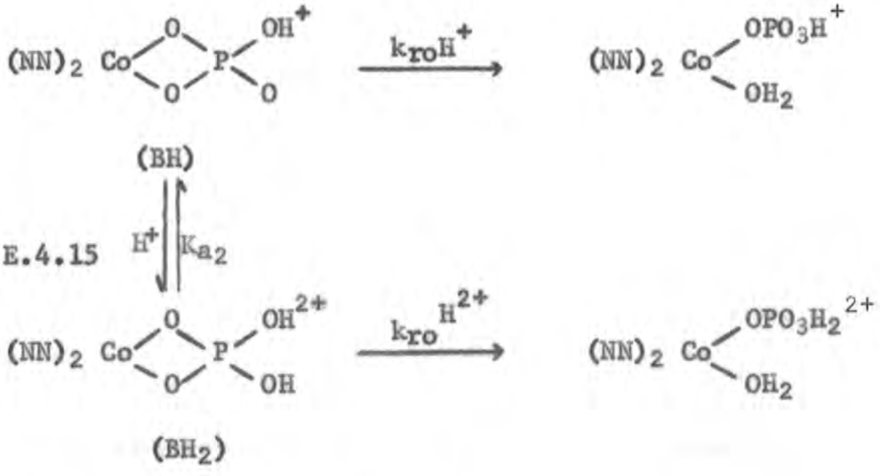
f_2 = fraction of $(Cotn_2(OH_2)PO_4H_2)^{2+}$

The approximate values for k_{ch}^D, k_{ch}^H and k_{ch}^o are 0.05 min^{-1}, 0.15 min^{-1} and 0.10 min^{-1} respectively. However, the variation in k_{ch} is very small and no great reliance may be placed on the absolute values of k_{ch}^D, k_{ch}^H and k_{ch}^o. The available data do suggest, however, that all of these rate constants are of similar magnitude.

4.4 Rate of Ring Opening of $Coen_2PO_4$ and $Cotn_2PO_4$ in Acid Concentrations up to 2.5M.

The ring opening reactions of the species $Coen_2PO_4$ and $Cotn_2PO_4$ were studied spectrophotometrically in the perchloric acid concentration range of 0.008M to 2.5M at 10°C and an ionic strength of 2.5. For the $Coen_2PO_4$ complex the reaction was followed at 550mμ, while for the $Cotn_2PO_4$, it was followed at 540mμ. First order rate plots were obtained.

The kinetic scheme for the high acid ring opening reactions is shown below



E.4.15

where NN represents en or tn.

Since 1st order kinetics are observed

E.4.16 $$\text{Rate} = k_{obs}\,(B_{tot}) = (k_{ro}^{H^{2+}}\,\alpha + (1-\alpha)k_{ro}^{H^{+}})(B_{tot})$$

E.4.17 $$\therefore\ (k_{obs} - k_{ro}^{H^{+}}) = k_{corr} = \alpha(k_{ro}^{H^{2+}} - k_{ro}^{H^{+}})$$

Defining K_{a_2} as the acidity constant

E.4.18 $$K_{a_2} = \frac{(H^+)(BH)}{(BH_2)}$$

i.e.

E.4.19 $$\frac{K_{a2}}{(H^+)} = \frac{(BH)}{(BH_2)}$$

then

E.4.20 $$1 + \frac{K_{a_2}}{(H^+)} = \frac{(B_{tot})}{(BH_2)} = \frac{1}{\alpha}$$

Substituting for α

E.4.21 $$\frac{1}{k_{corr}} = \left(1 + \frac{K_{a_2}}{(H^+)}\right)\left(k_{ro}^{H^{2+}} - k_{ro}^{H^+}\right)$$

E.4.22 $$\frac{1}{k_{corr}} = \frac{1}{\left(k_{ro}^{H^{2+}} - k_{ro}^{H^+}\right)} + \frac{K_{a_2}}{(H^+)\left(k_{ro}^{H^{2+}} - k_{ro}^{H^+}\right)}$$

The $k_{ro}^{H^+}$ values of 0.12 min^{-1} ($Coen_2PO_4$) and 0.087 min^{-1} ($Cotn_2PO_4$) at 10°C were calculated using $k_{ro}^{H^+}$ values at 22.5°C and 20.3°C and activation energies, E_{act}, of 13.7 $kcal.mole^{-1}$ and 14.6 $kcal.mole^{-1}$ for $Coen_2PO_4$ and $Cotn_2PO_4$ respectively.

By plotting $1/k_{corr}$ vs $\frac{1}{(H^+)}$, a straight line was obtained (Figs. 4.4 and 4.5). From the intercept and slope, values at 10°C for $k_{ro}^{H^+}$ and K_{a_2} are 25 ± 8 min^{-1} and 1.0 ± 0.3 for $Coen_2PO_4$ and 77 ± 10 min^{-1} and 0.37 ± 0.05 min^{-1} for $Cotn_2PO_4$. It is observed that diprotonation of both $Coen_2PO_4$ and $Cotn_2PO_4$ markedly increases the rate of opening of the phosphato chelate ring.

FIG. 4.4

HIGH ACID RING OPENING OF $Coen_2PO_4$

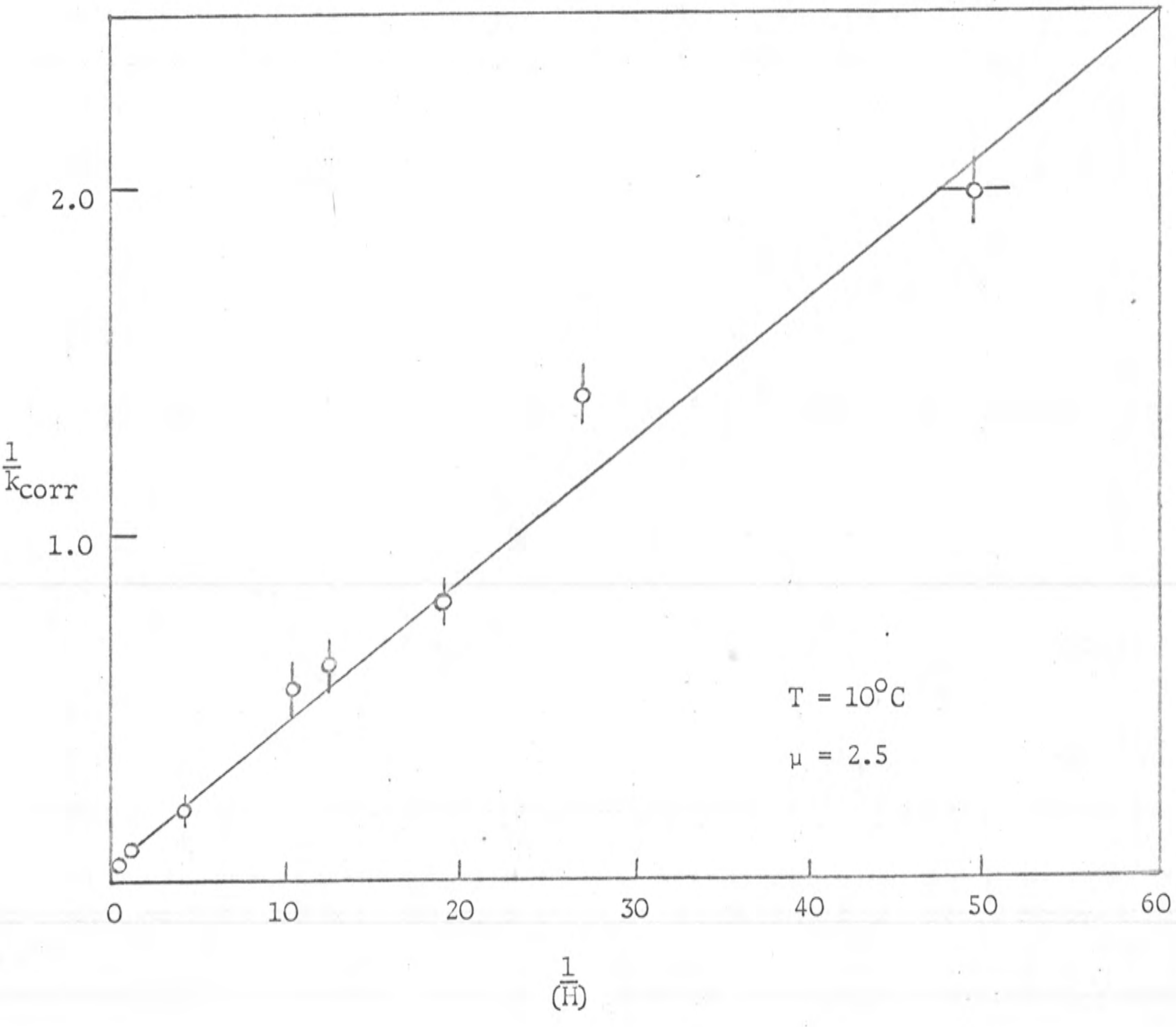


FIG. 4.5

HIGH ACID RING OPENING OF $Cotn_2PO_4$

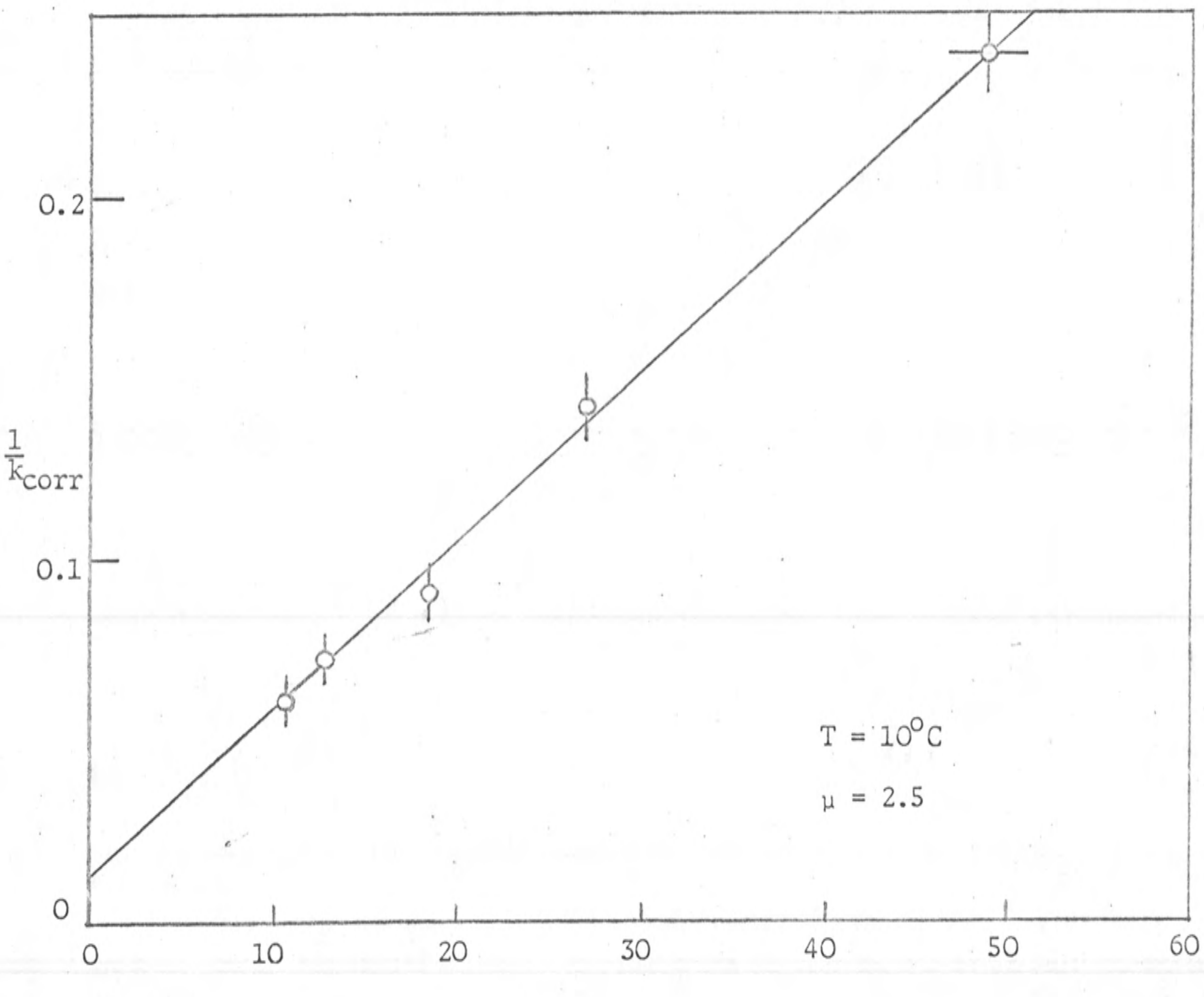


Table 4.3

Ring Opening of $Coen_2PO_4$ at High Acid Concentrations

T = 10°C μ = 2.5 ($NaClO_4$)

$(H^+)M$	$1/(H^+)$	$k(min^{-1})$	k_{corr}	$\frac{1}{k_{corr}}$
0.0031	3.2×10^2	0.19	0.069	14.5
0.020	49.8	0.62	0.50	1.99
0.037	27.1	0.83	0.71	1.41
0.054	18.4_5	1.39	1.27	0.79
0.079	12.6_5	1.73	1.61	0.62
0.095	10.5	1.91_5	1.79	0.56
0.25_7	4.0_5	5.1	5.00	0.20
0.83_5	1.2	11.0	10.89	0.09
2.47	0.4	20.0	19.92	0.05

Table 4.4

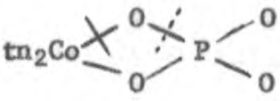
Ring Opening of $Cotn_2PO_4$ at High Acid Concentration

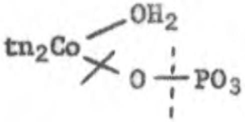
$T = 10^{o}C \quad \mu = 2.5\ (NaClO_4)$

$(H^+)M$	$1/(H^+)$	$k(min^{-1})$	k_{corr}	$\frac{1}{k_{corr}}$
0.0031	3.2×10^2	0.892	0.806	1.24
0.020	49.8	4.29	4.20	0.24
0.037	27.1	7.12	7.03	0.14
0.054	18.4_5	10.9	10.8	0.09
0.079	12.6_5	13.8	13.7	0.07
0.095	10.5	16.2	16.1	0.06

4.5 POSITION OF BOND CLEAVAGE OF $(Cotn_2PO_4)^o$ and $(Cotn_2(H_2O)PO_4)^o$

The two possible positions of bond cleavage in the ring opening and hydrolysis reactions of the bidentate and monodentate species are shown below:





If the ring opening and hydrolysis reactions are carried out in solvent enriched with H_2O^{18}, the actual positions of bond cleavage may be determined.

In the case of the hydrolysis of the monodentate species $(Cotn_2(H_2O)PO_4)^+$, depending on the position of bond cleavage, the equations can be represented thus:

E.4.23

$$\mathrm{tn_2Co}\begin{matrix}OH_2^0\\ O\text{-}PO_3\end{matrix} + H_2O^{18} \longrightarrow \mathrm{tn_2Co}\begin{matrix}OH_2^{3+}\\ O^{18}H_2\end{matrix} + PO_4^{\equiv}$$

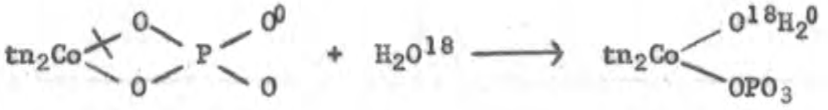
E.4.24

$$\mathrm{tn_2Co}\begin{matrix}OH_2^0\\ O\text{-}PO_3\end{matrix} + H_2O^{18} \longrightarrow \mathrm{tn_2Co}\begin{matrix}OH_2^{3+}\\ OH_2\end{matrix} + PO_3O^{18\equiv}$$

Hence if analyses are done on the O^{18}- enrichment in the phosphate products, it is possible to discriminate between two different reaction paths. The method of analysis is described in Section 7.6.1, Chapter 7.

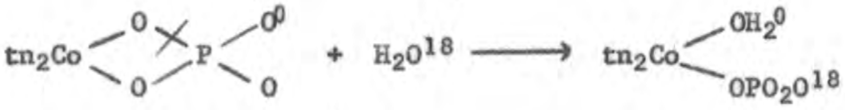
For the ring opening of the bidentate species, the following reaction schemes can be written

E.4.25



I

E.4.26



II

With a prior knowledge of the position of bond cleavage in the complete hydrolysis of the phosphato ligand from the cobalt (III) centre, the position of bond cleavage for the ring opening reaction may be deduced using a similar approach.

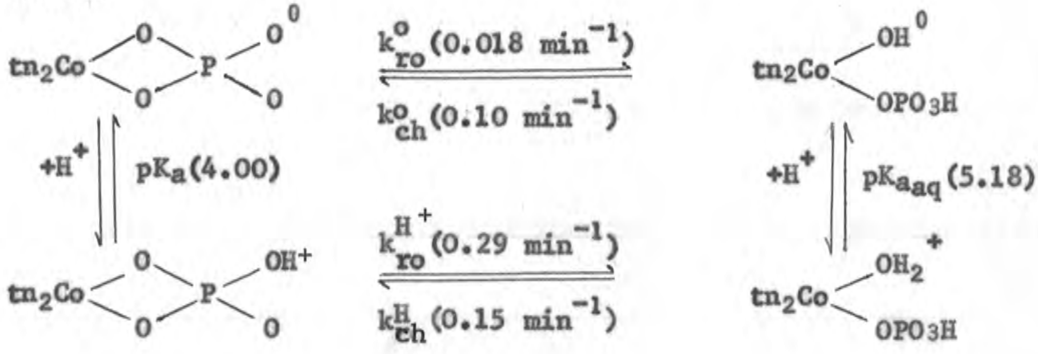
If complete Co-O bond cleavage occurs in the complete hydrolysis of I and II, then the phosphate products will be $PO_4^{\equiv}$ $PO_3O^{18\equiv}$ respectively. Therefore, if the Co-O bond is cleaved in both stages, no O^{18}-enrichment will be detected in the phosphate product.

It was found in the complete hydrolysis of $Cotn_2PO_4$ at 1.17M perchloric acid and 56°C, that there was less than 1% O^{18}-enrichment in the phosphate product. The percentage of O^{18} found in the released phosphate is 0.209 ± 0.007 atom percent. The O^{18} content of natural water analysed in the same manner was found to be 0.204 ± 0.002 atom percent. Other experiments have shown that the $PO_4^{\equiv}$ anion does not undergo any exchange under the same experimental conditions[30], as shown by blank runs in H_2O^{18}. Hence it was concluded that virtually complete Co-O bond cleavage occurs in both the ring opening and hydrolysis steps.

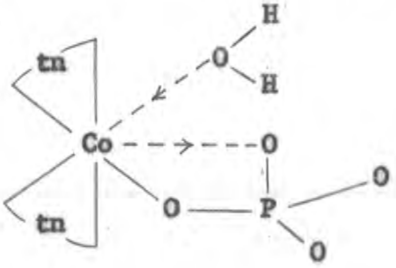
4.6 Discussion

Ring opening of $Cotn_2PO_4$ in pH range 3 to 5 occurs via the following scheme

E.4.27



For the acid catalysed path, a value of 0.29 ± 0.02 min^{-1} was obtained for $k_{ro}^{H^+}$. Lincoln[32] obtained a $k_{ro}^{H^+}$ value of 0.24 min^{-1} (corrected to 20.3°C) for the monoprotonated $Coen_2PO_4$. It appears that increasing the size of the amine chelate ring has little effect on the rate of ring opening of the monoprotonated phosphate ring. Furthermore, the results show that the ring opening of the chelate occurs more rapidly than the release of the phosphato ligand in the $Cotn_2PO_4$ system. This appears to be due to the strained character of the 4-membered phosphate chelate ring. (This effect is clearly shown for diprotonated bidentate phosphato, discussed below.) It is most likely that protonation of the phosphate chelate will occur on one of the 'exposed' oxygen atoms. Hence any intramolecular labilisation of the cobalt-oxygen bonds will be transmitted via the phosphorus atom. The charge on the complex changes from zero to one with protonation, and this increases the degree of solvation of the phosphato ligand. It is to be expected with the combination of these additional effects in the protonated bidentate, that the rate of ring opening will be considerably increased compared to the unprotonated bidentate. A concerted mechanism involving cis-attack of water would appear to be favourable for the acid-catalysed path.



In the high acid range, ring opening of the diprotonated bidentate phosphate ligand is described by the rate constant, $k_{ro}^{H^{2+}}$. For the species $(Coen_2PO_4H_2)^{2+}$, $k_{ro}^{H^{2+}}$ is 25 ± 8 min^{-1} and for $(Cotn_2PO_4H_2)^{2+}$, $k_{ro}^{H^{2+}}$ equals 77 ± 10 min^{-1} at 10°C. It is obvious that the diprotonated species, in both the bis(ethylenediamine) and the bis(trimethylenediamine) systems undergo ring opening much more rapidly than the monoprotonated species. For the $Coen_2PO_4$ system there is a 200 fold increase. The second proton would most probably be attached to the other 'exposed' oxygen atom. This would induce further labilisation of the cobalt-oxygen bond. Also on further protonation of the monoprotonated bidentate, the charge of complex is increased from +1 to +2. This would in turn increase the degree of solvation of the phosphato ligand. Hence it would be expected that the rate of ring opening should be enhanced. An even larger labilisation (600 fold) occurs with diprotonated bidentate $Cotn_2PO_4H_2{}^{2+}$.

The activation energies for ring opening of both $Coen_2PO_4H_2{}^{2+}$ and $Cotn_2PO_4H_2{}^{2+}$ were determined at acid concentrations 0.084M and 0.020M respectively, at which diprotonation is not complete. Hence the observed rate constant for ring opening, k_{ro}^{obs}, is given by

$$\text{E.4.28} \qquad k_{ro}^{obs} = k_{ro}^{H^{2+}} \frac{(CoN_2PO_4H^{+})(H^{+})}{K_{a_2}}$$

where N = en or tn. Thus the temperature dependence of k_{ro}^{obs} gives an apparent activation energy, E_{act}^{obs}, equivalent to the true activation energy for $k_{ro}^{H^{2+}}$ ($E_{act}^{H^{2+}}$) minus the enthalpy of ionisation for K_{a_2} (ΔH_{i_2})

E.4.29 i.e. $E_{act}^{obs} = E_{act}^{H^{2+}} - \Delta H_{i2}$

The values of ΔH_{i2} are unknown for the bidentate phosphato complexes. However, for the monodentate complexes, enthalpies of ionisation are 4.8 kcal.mole^{-1} ($Cotn_2(OH_2)PO_4$) and 3.7 - 7.7 kcal.mole^{-1} ($Coen_2(OH_2)PO_4$); a mean value of 5.7 kcal.mole^{-1} will be assumed for the latter system. Hence it may be estimated that the activation parameters for the diprotonated bidentate phosphate ring opening reaction are as shown in Table 4.5.

Table 4.5

Activation Parameters

Complex	(H^+) M	E_{act}^{obs} kcal.mole^{-1}	$E_{act}^{H^{2+}}$ kcal.mole^{-1}	$\Delta H^{\neq}$ kcal.mole^{-1}
$Cotn_2PO_4$	0.084	14.6 ± 0.2	19.4	18.8
$Coen_2PO_4$	0.020	13.7 ± 0.7	19.4	18.8

In each case, the O^{18}- tracer studies have conclusively demonstrated that the ring opening reaction involves 100% Co-O bond rupture. These activation parameters can therefore be compared to the values for Co-O bond rupture for hydrolysis of the monodentate phosphato complex. These values are $\Delta H^{\neq} = 25.0$ ($Coen_2(OH_2)PO_4$) and

$\Delta H^{\neq} = 26.1$ ($Cotn_2(OH_2)PO_4$). The distinctly lower values for Co-O bond rupture of a four membered phosphato ring very likely arise from the strained nature of this phosphato ring. The rapid ring opening reactions of both bidentate phosphato complexes can therefore be attributed to this strain energy of the phosphato chelate.

In the $Cotn_2PO_4$ system, there will be a greater S_N1 character in the transition state than in the $Coen_2PO_4$ system. The tendency to form a five-coordinated transition state would be related to the enhanced stability of the tn ligands which are sterically crowded in the six-coordinated reactant state and are forced to assume a single conformation.

CHAPTER 5

HYDROLYSIS REACTIONS OF PHOSPHATO-BIS(TRIMETHYLENEDIAMINE) COBALT (III)

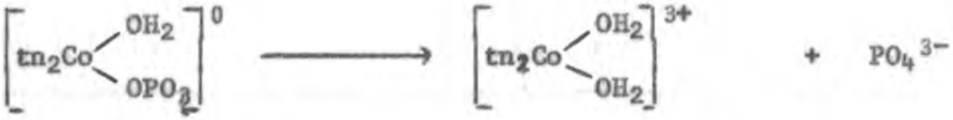
5.1 Introduction

The hydrolysis of the complexes $Co(NH_3)_5PO_4$, cis- $Co(NH_3)_4OH_2PO_4$ and cis- $Co(en)_2OH_2PO_4$ in acid and basic media has been studied[33] [34]. The object of studying the hydrolysis reactions of $Cotn_2PO_4$ is to observe the effects of increasing the ring size of the non-participating ligands on the rates of phosphate hydrolysis.

5.2 Hydrolysis in perchloric acid media

The complete hydrolysis of the phosphato ligand from $(Cotn_2PO_4)^0$ in aqueous perchloric acid occurs in two steps

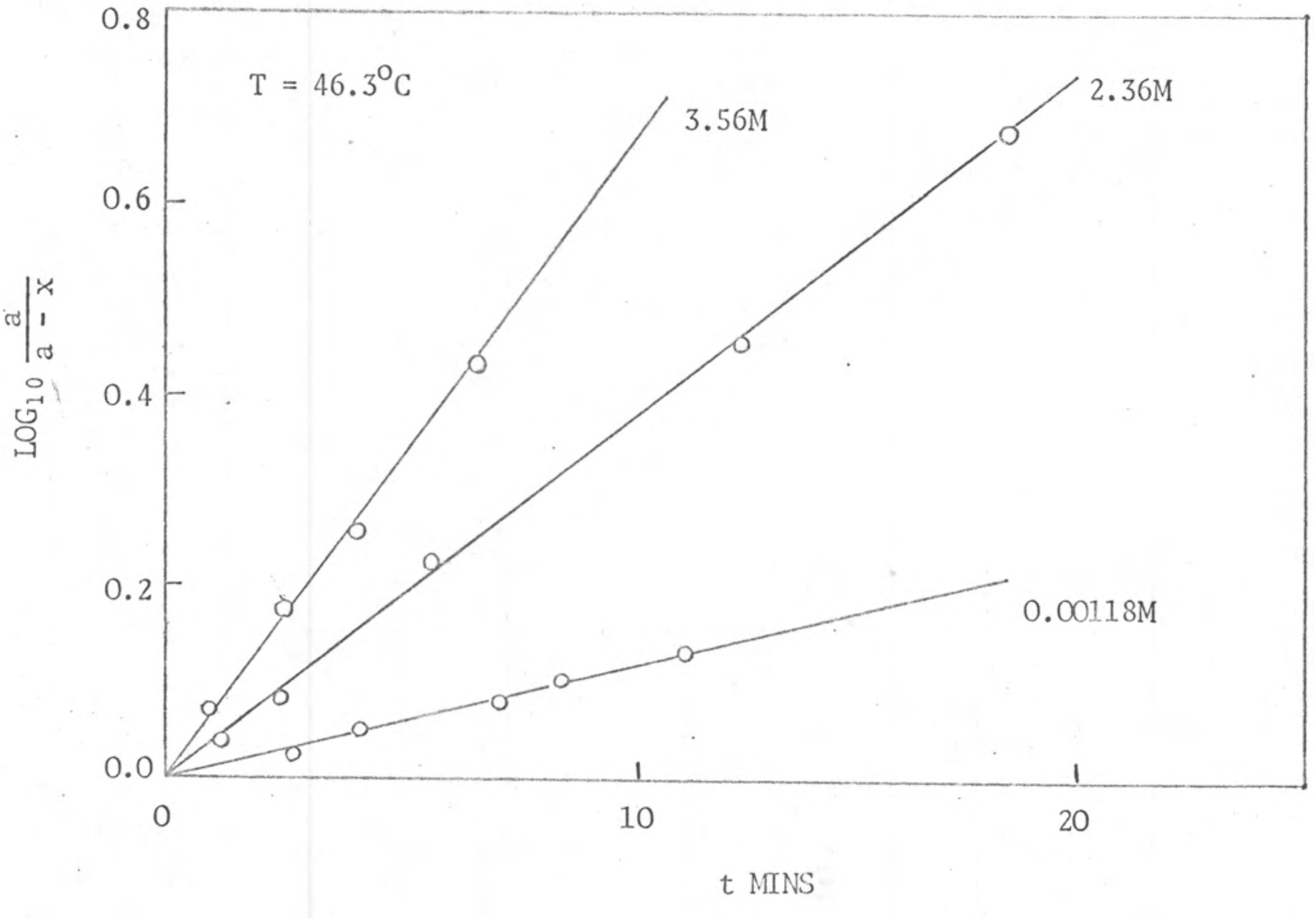
E.5.1 

E.5.2 

The ring opening reaction (E.5.1), is much more rapid than the hydrolysis reaction (E.5.2). Hence by studying the reaction with P^{32} labelled $Cotn_2PO_4$ in excess acid concentration, the hydrolysis reaction may be followed. Under these conditions, the reaction is first order in complex concentration. Good first order rate plots were obtained in all cases (Fig. 5.1). The observed rate constants, k_{obs},

FIG. 5.1

TYPICAL FIRST ORDER RATE PLOTS



for hydrolysis in the perchloric acid range of 0.001M to 11M at 46.3°C are tabulated in Table 5.1. The values of k_{obs} can be reproduced within ±5%. Fig. 5.2 shows the dependence of rate of hydrolysis on acid concentration.

By studying the reaction at various temperatures at 3.54M and 10.62M $HClO_4$, and plotting log k_{obs} vs. 1/T (Fig. 5.3), the activation energy, E_a, for the respective acid concentration may be determined. The activation parameters are collected in Table 5.2.

Table 5.1

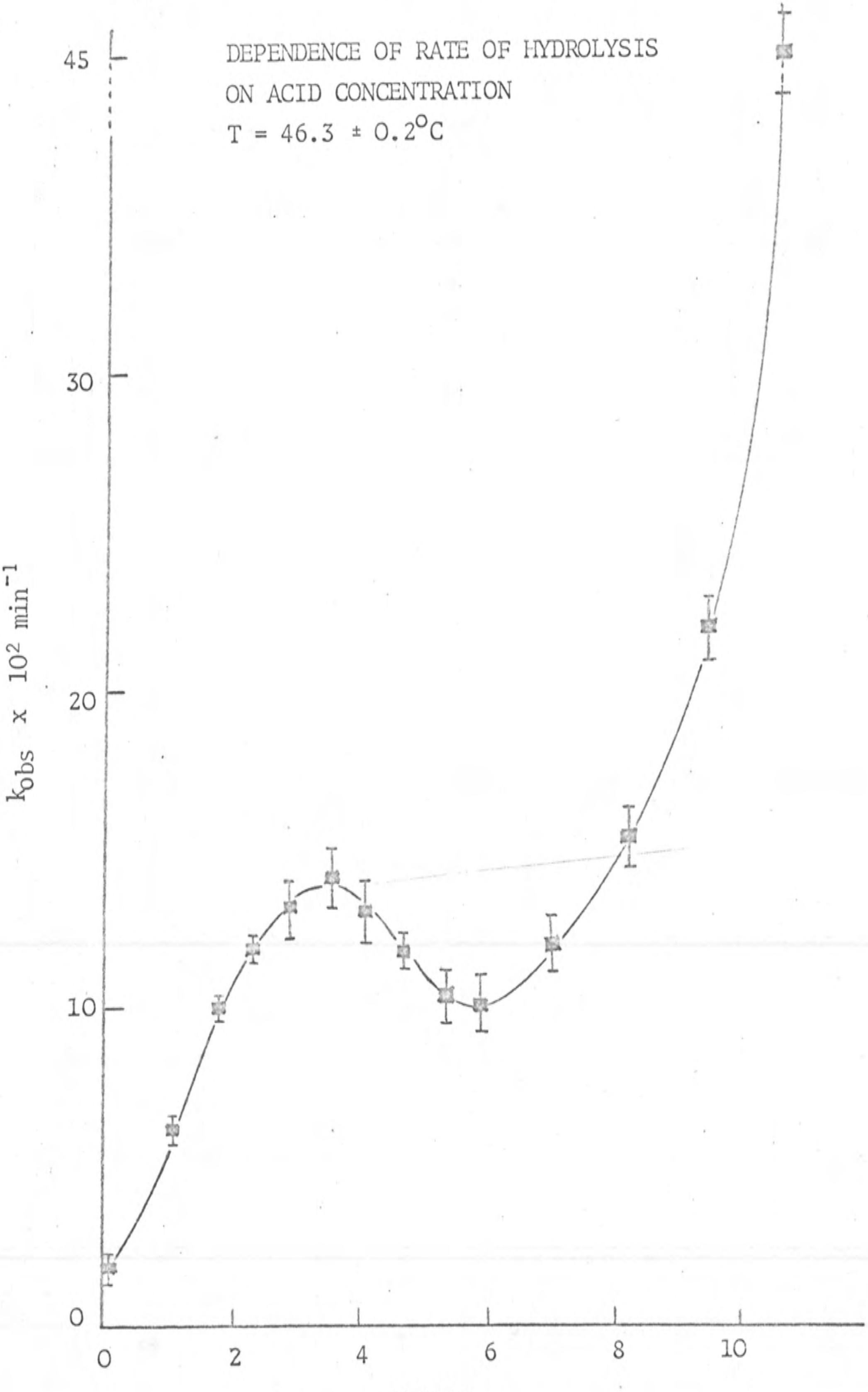
Observed Acid Hydrolysis Rates at 46.3°C.

M. $HClO_4$	$k_{obs} \times 10^2$ min^{-1}	$t_{\frac{1}{2}}$ min.
0.0118	2.6	27.2
0.0413	1.6	43.3
0.118	1.7	40.3
1.18	6.2	11.3
1.77	10.1	6.9
2.36	11.8	6.0
2.95	13.0	5.3
3.54	14.0	4.6
4.13	13.0	5.3
4.72	11.7	5.9
5.31	10.4	6.7
5.90	10.1	6.9
7.08	12.0	5.8
8.26	15.0	4.6
9.44	22.0	3.2
10.62	45.0	1.6
0.0012†	2.6	26.4
0.0029*	2.9	24.3

† (Complex) = 1.5×10^{-4}M * (Complex) = 2.6×10^{-4}M

All other complex concentrations are 1.2×10^{-3}M

FIG. 5.2



DEPENDENCE OF RATE OF HYDROLYSIS
ON ACID CONCENTRATION
T = 46.3 ± 0.2°C
k_{obs} x 10^2 min^{-1}
45
30
20
10
0
0
2
4
6
8
10
M $HClO_4$

FIG. 5.3

ACTIVATION ENERGIES IN AQUEOUS $HClO_4$

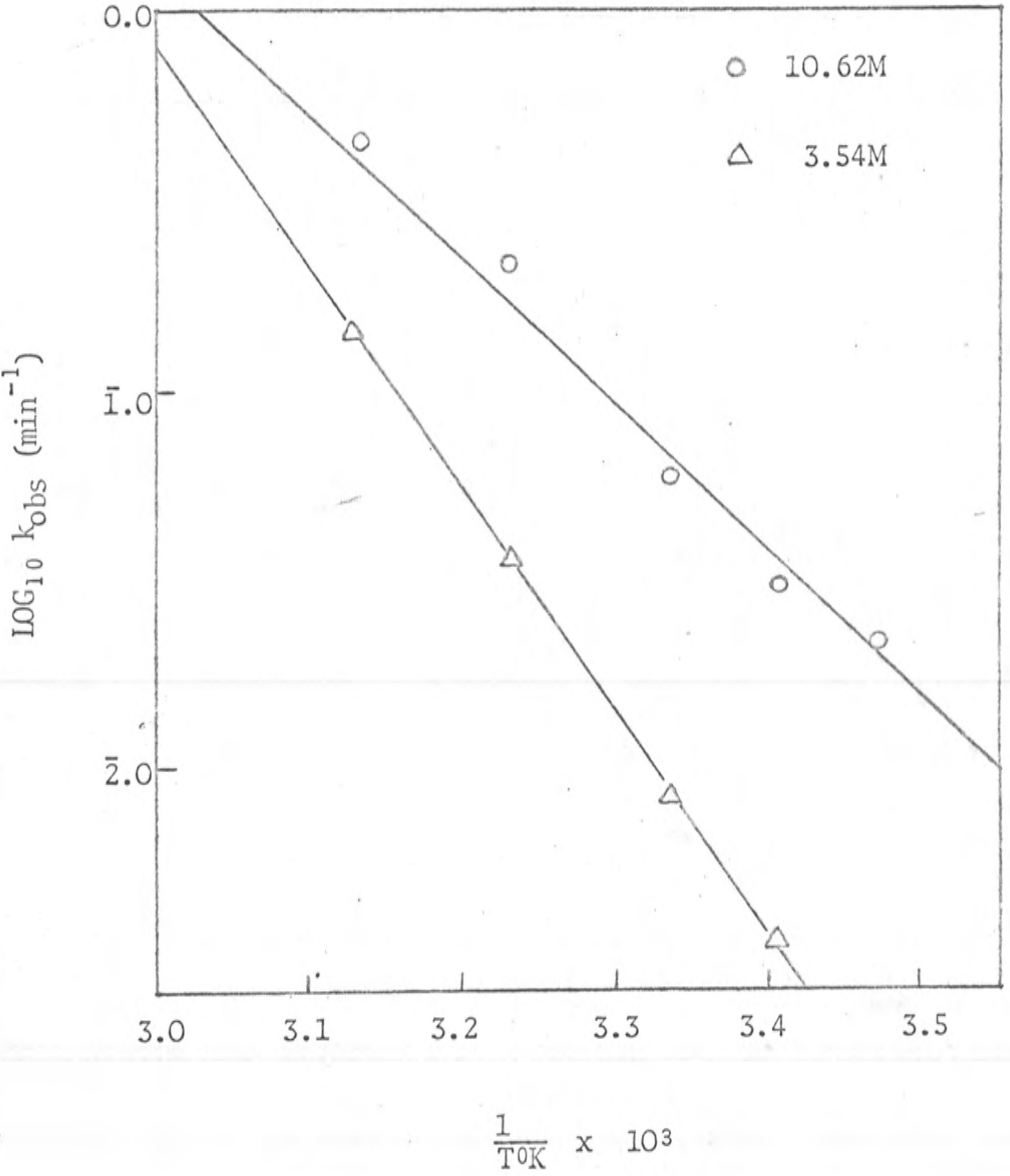


Table 5.2

Activation Parameters

M. $HClO_4$	E_a kcal.mole^{-1}	$\Delta H^{\neq}$ kcal.mole^{-1}	$\Delta S^{\neq}$ (46.3°C) e.u.
3.54	26.7 ± 0.3	26.1 ± 0.3	+5 ± 1
10.62	18 ± 1	17 ± 1	−22 ± 3

5.3 Base Hydrolysis

In basic media, the release of P^{32} labelled phosphate from the complex was followed in the concentration range of 10^{-3}M to 0.3M sodium hydroxide. Since the reaction was studied in excess hydroxide ion concentration, a psuedo first order rate law was observed. $NaClO_4$ was used to maintain the ionic strength of the reaction mixtures at unity. Good first order rate plots were obtained (Fig. 5.4). The observed rate constants are shown in Table 5.3. Fig. 5.5 illustrates the dependence of the rate of hydrolysis on hydroxide ion concentration. A linear relationship can be seen with a positive intercept on the k_{obs} axis. This is attributed to the existence of two composite terms for the observed rate, one independent of the hydroxide ion concentration and the other dependent linearly on the hydroxide ion concentration.

FIG. 5.4

TYPICAL FIRST ORDER RATE PLOTS

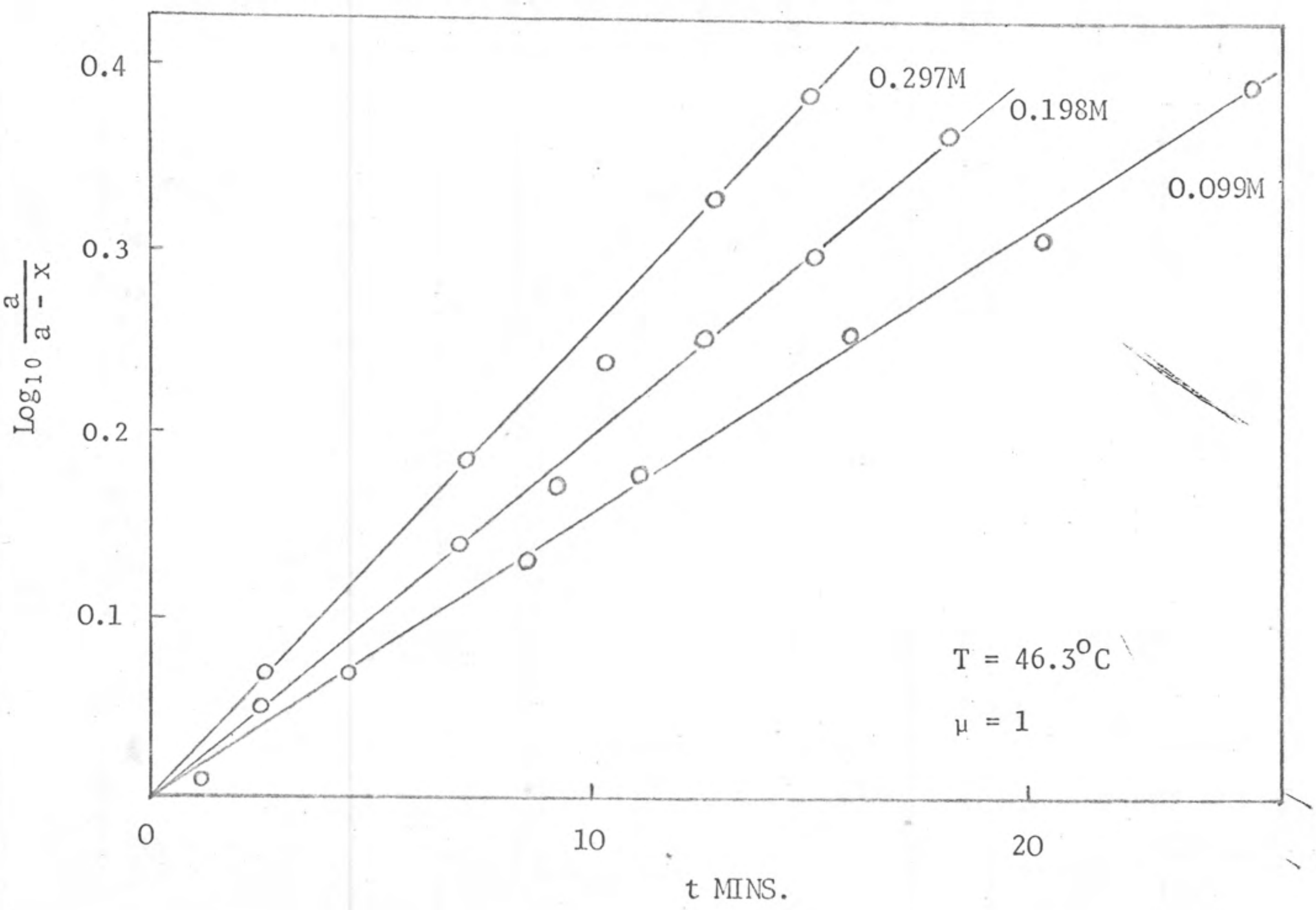


Table 5.3

Observed Base Hydrolysis Rates at 46.3°C

M. NaOH	$k_{obs} \times 10^2$ min^{-1}	$t_{\frac{1}{2}}$ min.
0.99×10^{-3}	0.72	96.3
0.05	2.7	26.3
0.099	3.4_5	19.4
0.198	4.5	15.4
0.297	6.1	11.4

Hence,

E.5.3 $k_{obs} = k_1 + k_2(OH^-)$

From the intercept and slope in Fig. 5.5, k_1 and k_2 may be evaluated (Table 5.4).

By studying the temperature dependence of the rate of base hydrolysis, the activation parameters for the two paths may be determined from the respective values of k_1 and k_2 (Table 5.5).

FIG. 5.5

DEPENDENCE OF k_{obs} ON (OH^-)

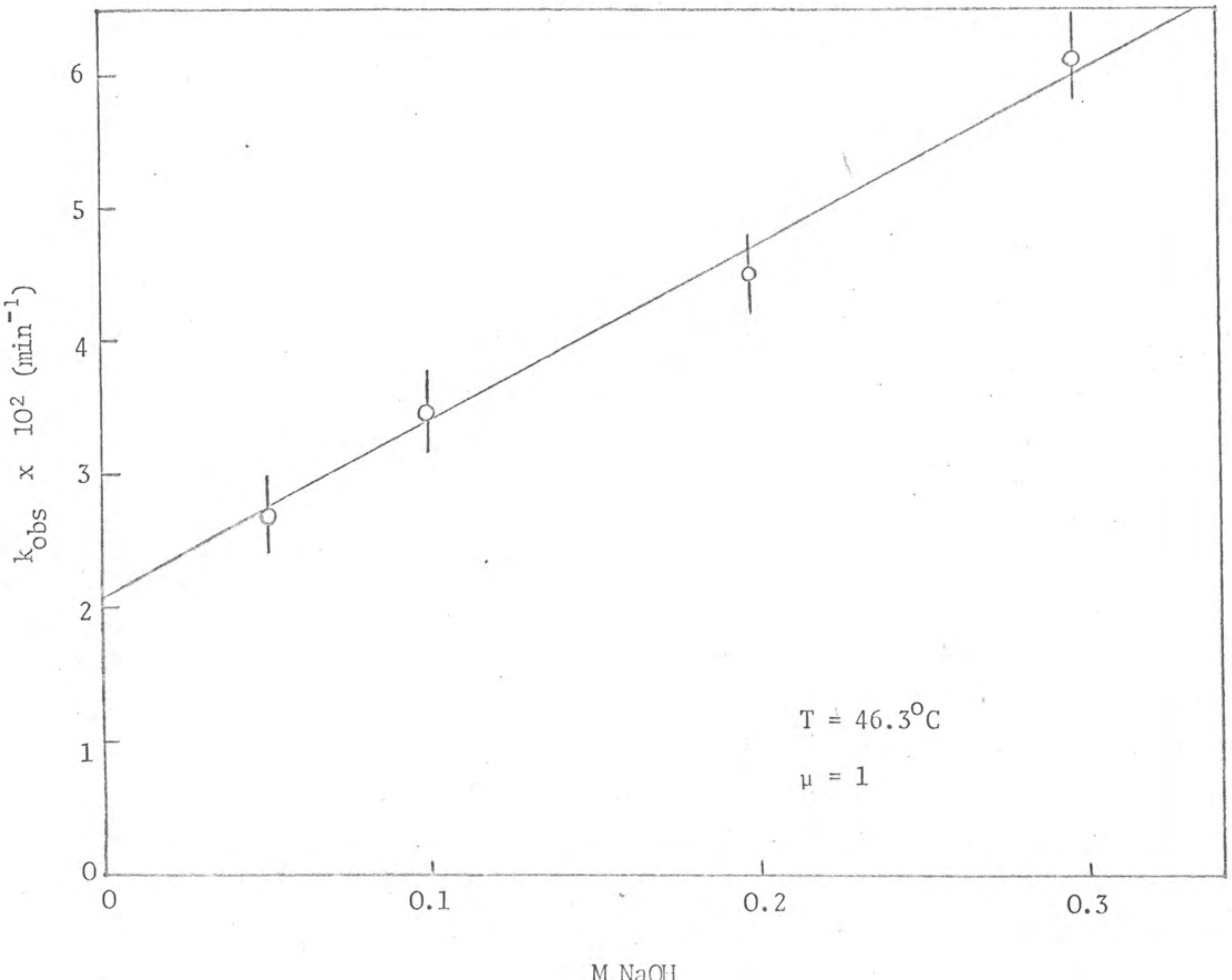


Table 5.4

Values for k_1 and k_2

Temp °C	$k_1 \times 10^2$ min^{-1}	$k_2 \times 10^2$ min^{-1}
54.9 ± 0.1	6.9 ± 1.0	18 ± 3
46.3 ± 0.1	2.0 ± 0.3	14 ± 2
36.35 ± 0.15	0.62 ± 0.09	3.3 ± 0.4
26.7 ± 0.1	-	0.92 ± 0.15

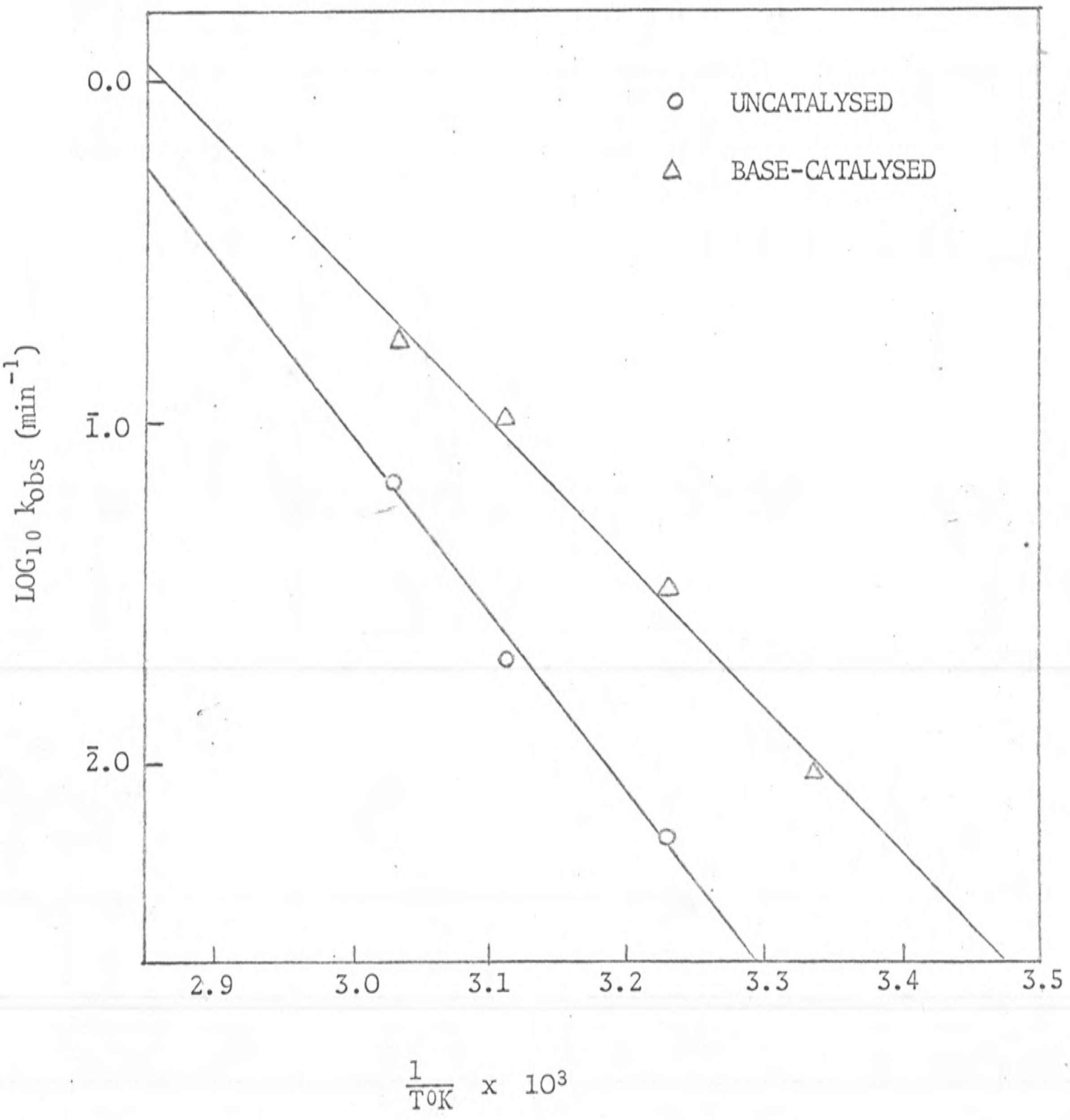
Table 5.5

Activation Parameters for Base Hydrolysis at 46.3°C

E_{a_1} kcal mole^{-1}	$\Delta H_1^{\neq}$ kcal mole^{-1}	$\Delta S_1^{\neq}$ eu	E_{a_2} kcal mole^{-1}	$\Delta H_2^{\neq}$ kcal mole^{-1}	$\Delta S_2^{\neq}$ eu
23.8 ± 0.7	23.2 ± 0.7	+0.8 ± 1.0	20 ± 3	20 ± 3	-16 ± 3

FIG. 5.6

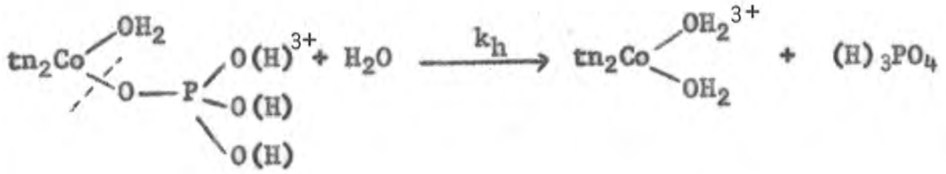
ACTIVATION ENERGIES FOR BASE HYDROLYSIS



5.4 Discussion

The release of phosphate from $Cotn_2PO_4$ in acid media may be described by the general equation

E.5.4



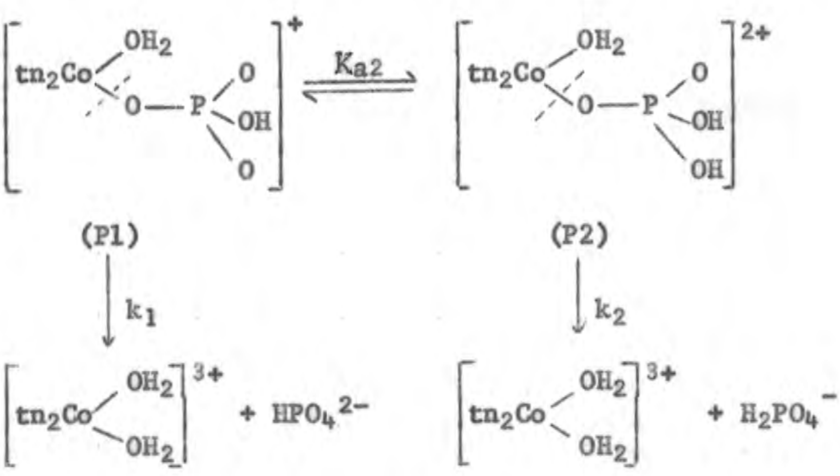
where (H) denotes the possible degree of protonation of the phosphato ligand. In perchloric acid, hydrolysis of the phosphato ligand is found to proceed via Co-O bond cleavage exclusively (see Section 4.5 Chapter 4). It is convenient to divide the acid concentration range into the following three regions

1) 0.001M - 0.04M,
2) 0.04M - 5M, and
3) 5M - 11M.

5.4.1 The acid concentration range 0.001M to 0.04M

In this region, the predominant species are the monoprotonated <u>cis</u>- $(Cotn_2(OH_2)OPO_3H)^+$ (P1) and the diprotonated <u>cis</u>- $(Cotn_2(OH_2)OPO_3H_2)^{2+}$ (P2) species. The rate of hydrolysis is governed by their individual rate constants, k_1 and k_2, and the acid-base equilibrium constant, K_{a_2}, that inter-relates the two species

E.5.5



The overall hydrolysis rate may be written

E.5.6 $$\text{Rate} = k_{obs}((P1) + (P2)) = k_1(P1) + k_2(P2)$$

Since the acidity constant, K_{a_2}, is defined as

E.5.7 $$K_{a2} = \frac{(P1)(H^+)}{(P2)}$$

then

E.5.8 $$k_{obs}\left(\frac{(P1) + (P2)}{(P2)}\right) = \frac{k_1K_{a_2}}{(H^+)} + k_2$$

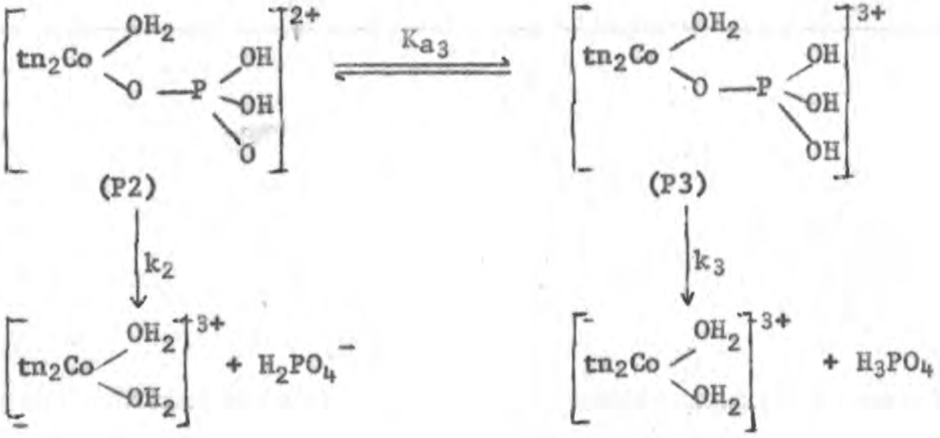
Using a pKa_2 value of 2.69 calculated assuming a ΔH value of 4.8 kcal/mole, and equations (E.5.7) and (E.5.8), k_1 and k_2 were evaluated to be 3.1×10^{-2} min^{-1} and 0.2×10^{-2} min^{-1} respectively at 46.3°C. Therefore the P1 species is ten times more reactive than the P2 species.

On the basis of protonation causing an inductive shift and a weakening of the cobalt-oxygen bond, the expected order of lability of the protonated phosphato ligands should be P2 > P1. The order of lability is found to be reversed in these studies. An additional labilising effect may arise from hydrogen bonding between the vicinal aquo and phosphato ligands. The partial hydroxo character of the aquo ligand may impart, by π-bonding effects, an enhanced lability of the cis- phosphato ligand. Bronsted[60] first observed the labilising effect on the hydroxo ligand in $Co(NH_3)_4OH.NO_3{}^+$ which hydrolysed 10^4 times faster than $Co(NH_3)_4OH_2NO_3{}^{2+}$. In the P2 species, two of the peripheral oxygen atoms are protonated which reduces the basicity of the remaining oxygen substantially. As a result, the hydrogen bonding effects between the aquo and phosphato ligands would be less important in the P2 species compared to the P1 species.

5.4.2 The acid concentration range 0.04M - 5M

Cis- $(Cotn_2(OH_2)OPO_3H_2)^{2+}$ (P2) and cis $(Cotn_2(OH_2)OPO_3H_3)^{3+}$ (P3) are the predominant species in this acid range. Both these complexes hydrolyse at characteristic rates.

E.5.9



The observed rate constant, k_{obs}, increases from 0.04M acid to a maximum at 3.5M. This maximum in the rate profile corresponds to the point at which the protonation of the P3 species is almost complete. Above 3.5M $HClO_4$, k_{obs} is observed to decrease in value. This decrease in rate is attributed to the fall in water activity with increasing perchloric acid concentration in this range (Fig. 5.7).

In Fig. 5.9, k_{obs}/a_{H_2O} is plotted against perchloric acid concentration[61]. A plateau region appears between the acid range of 3.5M to 5M. In this region, the phosphato complex exists solely as the P3 species and the rate law is

E.5.10 $$\text{Rate} = k_{obs\,(limiting)}\,(P3)$$

$$= k_3(P3)a_{H_2O}$$

A value of 1.83×10^{-1} min^{-1} was obtained for k_3 at 46.3°C. For the $Coen_2PO_4$ complex, k_3 (corrected to the same temperature) has a value of 2.91×10^{-2} min^{-1}.[33]

At acid concentrations less than 0.5M, the P2 species makes a significant contribution to the overall rate of hydrolysis. If the hydrolysis of P2 also exhibits a first order dependence upon a_{H_2O}, the overall rate law may be written

E.5.11 $$\text{Rate} = k_{obs}((P2) + (P3)) = k_2(P2)a_{H_2O} + k_3(P3)a_{H_2O}$$

where k_{obs} is the observed first order rate constant including the activity of water

$$\text{i.e.} \quad k_{obs} = k'_{obs} \cdot a_{H_2O}$$

FIG. 5.7

a_{H_2O} vs $(HClO_4)$ M

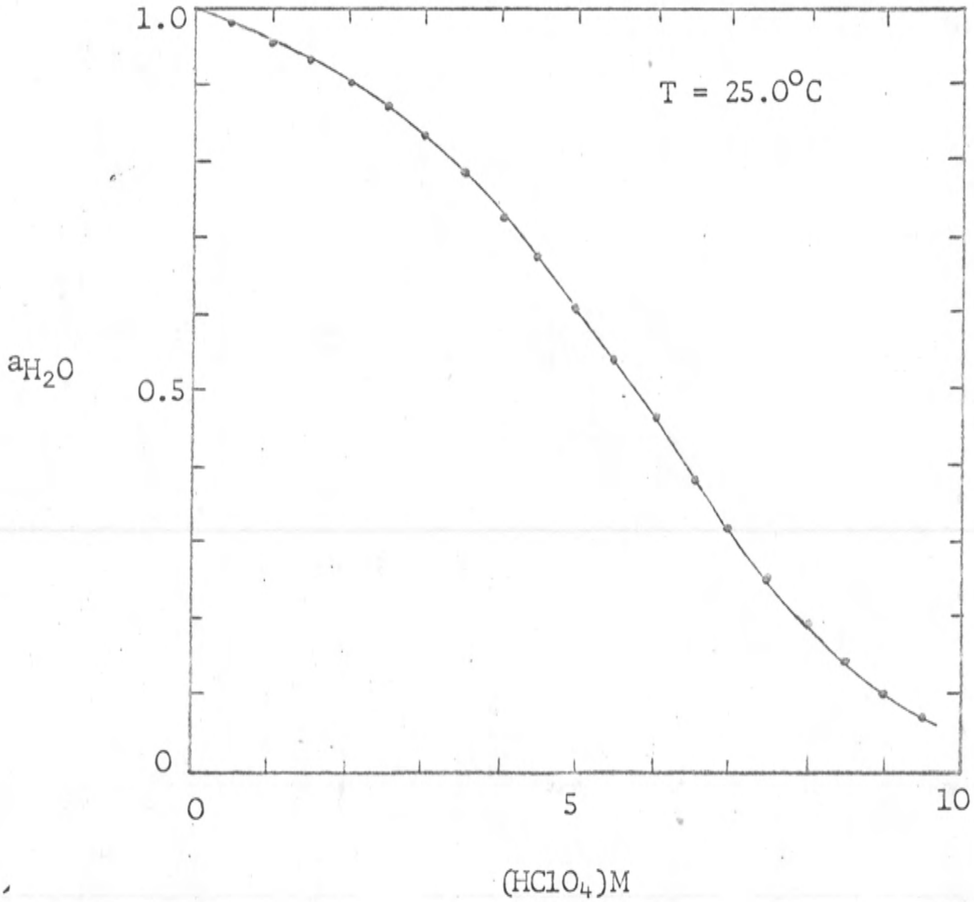


FIG. 5.8

HYDROLYSIS IN AQUEOUS PERCHLORIC ACID

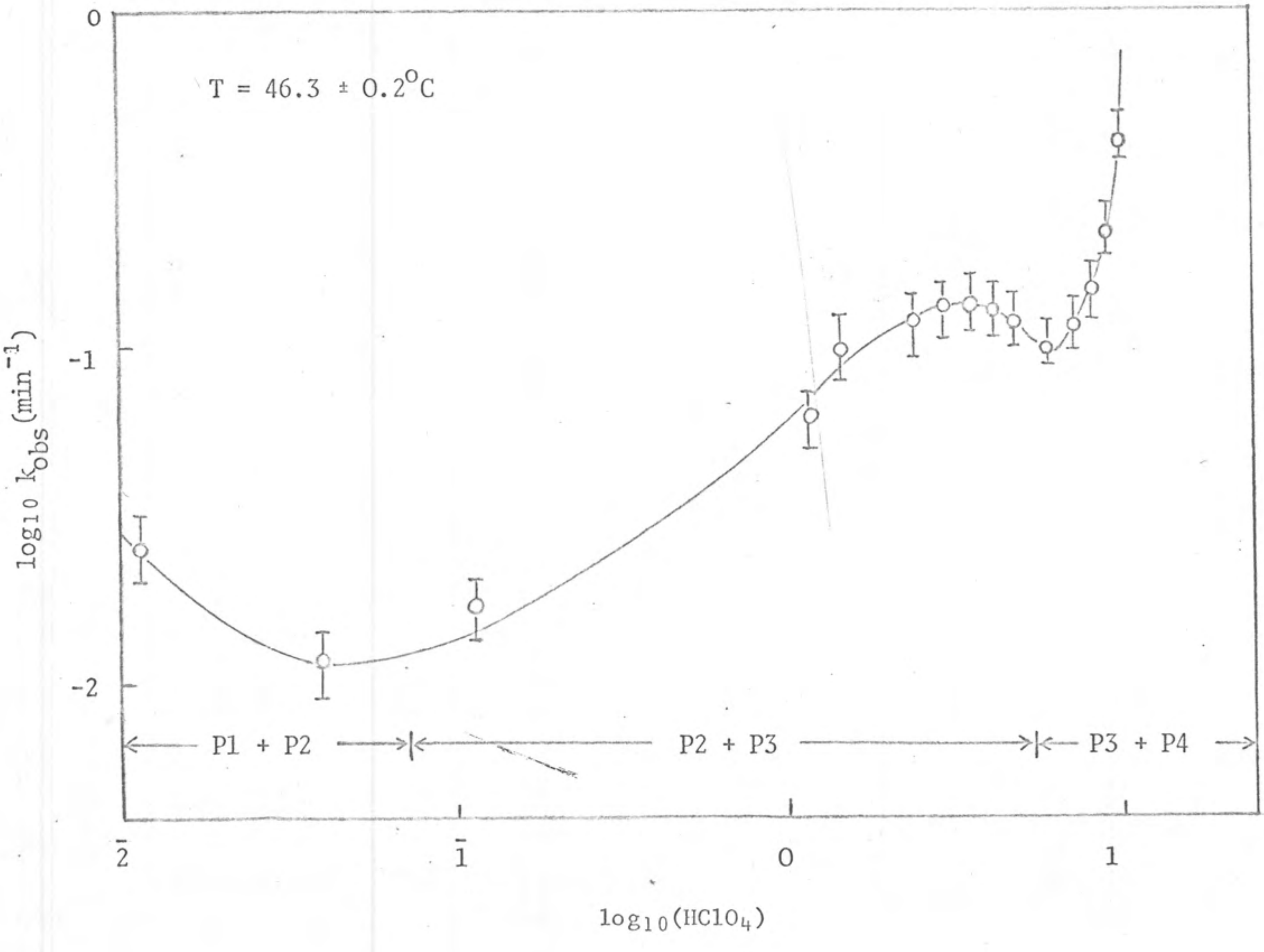
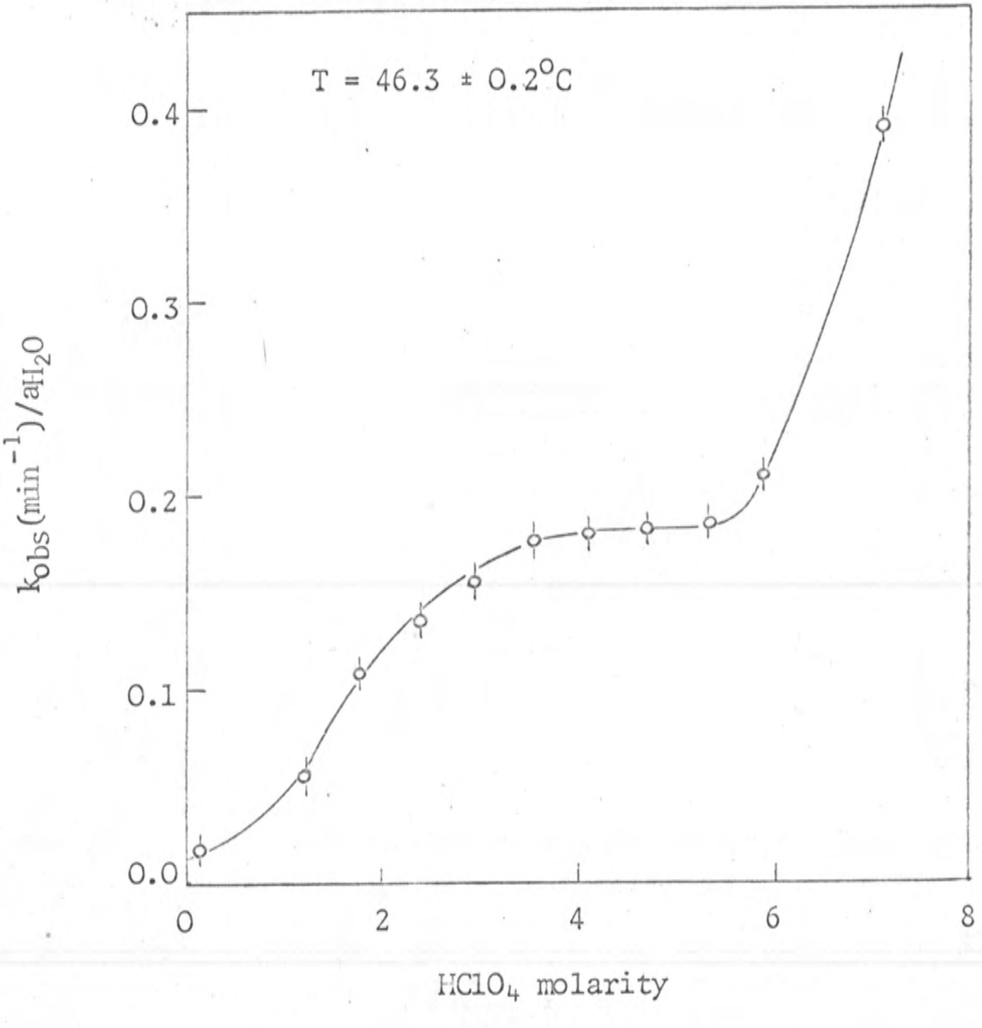


FIG. 5.9

DEPENDENCE OF RATE OF HYDROLYSIS ON ACTIVITY OF WATER



and

E.5.12 $$k_3 = \frac{k_{obs}(\text{limiting})}{a_{H_2O}}$$

as previously defined.

The activation energies and the derived activation parameters for the bis(trimethylenediamine), pentammine, tetrammine and bis (ethylenediamine) systems are shown in Table 5.6.

Table 5.6

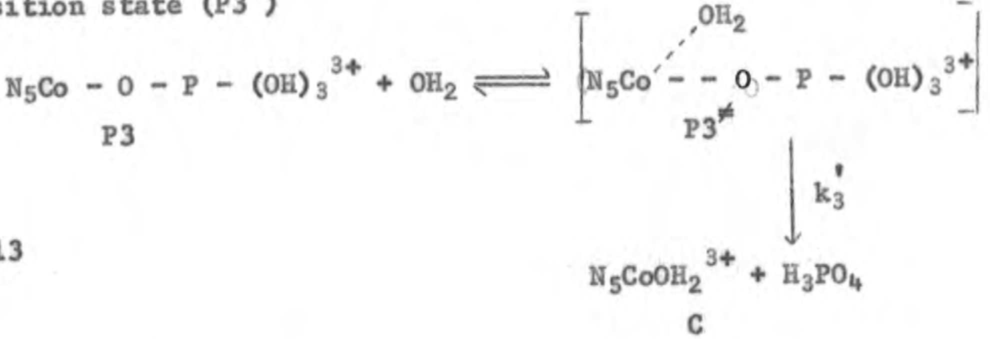
Activation Parameters for Phosphato Complex Ions

Complex	M $HClO_4$	E_{act}(kcal/mole)	$\Delta S^{\neq}$(eu)
pentammine*	4.11	26.3 ± 0.3	-7.4 (60°C)
tetrammine*	5.7	25.6 ± 0.3	-7.8 (60°C)
bis(en)*	4.0	25.6 ± 0.3	-8.3 (60°C)
bis(tn)†	3.54	26.7 ± 0.3	-3.4 (46.3°C)

*Lincoln and Stranks

†This work

The triprotonated species, $Co(NH_3)_5PO_4H_3{}^{3+}$, $Co(NH_3)_4(OH_2)PO_4H_3{}^{3+}$ and $Coen_2(OH_2)PO_4H_3{}^{3+}$, all show first order dependence on the activity of water in their rates of hydrolysis. A mechanism has been proposed[33] for the hydrolysis of these P3 complexes which involves SN2 attack of water upon the P3 species with a seven coordinated transition state ($P3^{\neq}$)



$$\underset{P3}{N_5Co-O-P-(OH)_3^{\;3+}} + OH_2 \rightleftharpoons \underset{P3^{\neq}}{\left[N_5Co\cdots O-P-(OH)_3\right]^{3+}} \xrightarrow{k_3'} \underset{C}{N_5CoOH_2^{\;3+}} + H_3PO_4$$

E.5.13

where N_5 is $(NH_3)_5$, $(NH_3)_4(OH_2)$ or $(en)_2(OH_2)$

The rate may be written

E.5.14 $\quad \text{Rate} = k_3'(P3^{\neq})f_{P3^{\neq}} = k_3(P3)f_{P3}a_{H2O}/f_{P3^{\neq}} = k_{obs}(P3)a_{H2O}$

Since no change in formal charge occurs on formation of the transition state, the activity coefficient ratio $f_{P3}/f_{P3^{\neq}} \approx 1$.

The formation of the bimolecular transition state $P3^{\neq}$ is accompanied by a decrease in entropy due to the disappearance of a molecule of water from solution. This decrease in entropy is estimated to be -7.9 eu[66] and is found to be consistent with the observed $\Delta S^{\neq}$ values for these three complexes (-7.4 to -8.3 eu). Since the $(Cotn_2(OH_2)PO_4H_3)^{3+}$ complex also exhibits a first order dependence on the activity of water, it is very probable that it hydrolyses via a similar mechanism.

The negative value of $\Delta S^{\neq}$(-3.4 eu) is slightly less negative than the values for the other complexes. If the Co-O bond in the transition state was extended this would allow a greater amount of freedom for the phosphato group. This will increase the number of vibrational degrees of freedom of the phosphato ligand. Also with the phosphato group further away from the cobalt (III) centre, the strained trimethylenediamine rings can expand or distort favourably in the less crowded transition state. Increases in entropy should result from all these processes. It would then appear that the bond breaking contribution to $\Delta H^{\neq}$ and $\Delta S^{\neq}$ would be more important in the bis(trimethylenediamine) complex compared to the other three complexes. However, bond making occurs to some extent in all cases as dependence on the activity of water is observed for the rates of hydrolysis. The rate of hydrolysis for the P3 species in the bis(trimethylenediamine) complex is 160 times greater than that of the bis(ethylenediamine) complex, which clearly indicates that steric crowding plays an important role in increasing the rates of hydrolysis in this acid region.

5.4.3 The acid concentration range 5M - 11M

Since the activity of water falls from 0.61 in 5M $HClO_4$ to 0.05 in 10M $HClO_4$,[61] the contribution to the overall hydrolysis rate due to the triprotonated complex should diminish sharply at these high acid concentrations. It is however, observed that k_{obs}/a_{H_2O} begins to increase above the plateau region at about 5.5M $HClO_4$. This is attributed to a fourth protonation stage occurring in the complex. The fourth proton may be added to the aquo ligand, the bridging phosphato oxygen or shared between the aquo ligand and the bridging phosphato oxygen of the aquo phosphato complex. Because of the marked acceleration of the rates of hydrolysis in this acid region, it is proposed that the fourth proton interacts directly with the bridging phosphato oxygen. This would be most effective in increasing the lability of the phosphato ligand.

Table 5.7

Activation Energies of Phosphato Complex Ions

Complex	M $HClO_4$	E_{act}(kcal $mole^{-1}$)
pentammine*	10.4	23.5 ± 0.3
tetrammine*	10.8	25.0 ± 0.3
bis(en)*	10.4	26.1 ± 0.5
bis(tn)†	10.62	17.7 ± 1.5

* Lincoln and Stranks

† This work

The observed activation energy for $Cotn_2PO_4$ hydrolysis in 10.6M $HClO_4$ is significantly less than the activation energy observed in 3.5M $HClO_4$, where the phosphato complex is completely protonated to the third stage. There is no evidence that even in 10.6M $HClO_4$ the rate of hydrolysis "levels off" and this suggests that only a small fraction of the phosphato complex is tetraprotonated. Hence to the observed activation energy must be added the enthalpy of ionisation, ΔH_{i_4}, of the tetraprotonated complex to give the true activation energy. A minimum value of 4.8 kcal mole^{-1} probably applies so that the true activation energy for hydrolysis of the tetraprotonated species is not less than 22.5 kcal mole^{-1}. In the case of tetrammine and ethylenediamine complexes, activation energies are very similar in both 4M and 10M $HClO_4$. This would suggest that the enthalpies of ionisation of these phosphato complexes are much smaller than for the trimethylenediamine complex.

5.4.4 Base hydrolysis in 10^{-3}M to 0.3M NaOH

In basic media, the overall rate law for the release of phosphate is

E.5.15 $\text{Rate} = k_1(\text{Complex}) + k_2(\text{Complex})\,(OH^-)$

where k_1 is a first order rate constant pertaining to the uncatalysed hydrolysis reaction of cis-$(Cotn_2(OH).PO_4)^{1-}$, and k_2 is a second order rate constant pertaining to the base catalysed hydrolysis reaction of the same species.

5.4.5 Uncatalysed base hydrolysis

Considerable labilisation of the phosphato ligand is observed for the cis-hydroxophosphato complex ions compared to the pentammine complex. The presence of a π-bonding hydroxo ligand cis- to the leaving phosphato group is expected to cause this effect.[60] The values of k_1 are listed in Table 5.8. This labilising effect is greatly enhanced in $(Cotn_2(OH).PO_4)^{1-}$ where a 70 fold increase in the rate hydrolysis is observed compared to that of $(Coen_2(OH).PO_4)^{1-}$. Relief of ring strain to form a five coordinated species is highly favourable for the $(Cotn_2(OH).PO_4)^{1-}$ species. The greater lability of the tetrammine species compared to the bis(ethylenediamine) species

Table 5.8

Rate constants for Uncatalysed Base Hydrolysis and corresponding Activation Parameters of Phosphato amine cobalt (III) complex ions

$\mu = 1$ Temp. 55°C

Complex Ion	$k_1 \times 10^3 (min^{-1})$	$\Delta H_1^{\neq}(kcal\ mole^{-1})$	$\Delta S_1^{\neq}(eu)$
t[a]	51.4	26.7	-0.19
en[a]	1.1	28.8	-3.3
tn[b]	68.8	23.2	+0.8

t = $(Co(NH_3)_4(OH).PO_4)^-$, en = $(Coen_2(OH).PO_4)^-$,
tn = $(Cotn_2(OH).PO_4)^-$

a Values from Lincoln S.F., Ph.D. Thesis corrected to 55.5°C.

b Values obtained in this work.

has been explained in terms of the greater stabilisation of the tetrammine transition state owing to greater solvation. The $(\mathrm{Cotn_2(OH).PO_4})^{1-}$ species appear to be more labile than the tetrammine species and this may be again ascribed to the relief of ring strain.

The activation energy, E_{a1}, for the tetrammine species is slightly smaller than that of the bis(ethylenediamine) species. An S_N2 water attack mechanism has been proposed for these systems.[34] The most significant effect of introducing the trimethylenediamine ligands is to reduce the enthalpy of activation for hydrolysis of phosphate from the hydroxophosphato complex. The lower value of $\Delta H^{\neq}$ would be consistent with a sterically strained trimethylenediamine complex with a reduction of this strain on forming the transition state. It would be expected that the transition state will have less S_N2 character than for the tetrammine and bis(ethylenediamine) complexes.

5.4.6 Base catalysed hydrolysis

The linear dependence of rate upon hydroxide ion concentration for the hydroxophosphato species may arise via two mechanisms.

1) SN1CB in which a five coordinated intermediate is produced in a rapid proton base equilibrium and competed for by PO_4^{3-}, OH^- and H_2O.

2) S_N2 in which the rate determining step is the formation of a seven coordinated intermediate between the hydroxide ion and the hydroxo-phosphate complex ion.

Lincoln[30] argues against an S_N1 mechanism by comparing the ratios of k_1/k_2 for the $(Co(NH_3)_4(OH).PO_4)^{1-}$ and the

Table 5.9

Base Catalysed Rate Constants and corresponding Activation Parameters of Phosphato-amine cobalt (III) complex ions

$\mu = 1$ Temp = 55°C

Complex Ion	$k_2 \times 10^3 M^{-1} min^{-1}$	$\Delta H_2^{\neq}$ kcal mole^{-1}	$\Delta S_2^{\neq}$ eu
p[a]	28.7	35.0	+24.2
t[a]	22.1	28.6	-4.1
en[a]	6.2	29.0	+2.6
tn[b]	176.0	19.5	-16.3

p = $(Co(NH_3)_5PO_4)^0$, t = $(Co(NH_3)_4(OH).PO_4)^-$

en = $(Coen_2(OH).PO_4)^-$ tn = $(Cotn_2(OH).PO_4)^-$

a Values from Lincoln S.F., Ph.D. Thesis corrected to 55°C.

b Values obtained in this work.

$(Coen_2(OH).PO_4)^{1-}$. If the five coordinated species $(CoN_4OH)^{2+}$ is formed, the relative affinities for H_2O and OH^- is not expected to change markedly when N = NH_3 is replaced by N = en but a great change was observed. (k_1/k_2 (tetrammine) = 2.33, k_1/k_2(bis (ethylenediamine)) = 0.18). However, this is the expected order on the grounds of electro static repulsion between the hydroxophosphato ion and the attacking hydroxide ion. The charge density on the larger bis(ethylenediamine) complex ion will be least and the consequent interionic repulsion will therefore be least. This is compatible with S_N2 reaction. The S_N2 mechanism appears also to be consistent for the bis(trimethylenediamine) case as the ratio k_1/k_2 is 0.39. The greater rate of base catalysed hydrolysis of tetrammine compared to that of bis(ethylenediamine) is attributed to solvation effects in the transition state. Comparatively, the bis(trimethylenediamine) hydrolyses even faster than tetrammine which indicates that steric effects are more important than solvation effects.

5.5 General Conclusions

The importance of protonation in affecting the reactivity is demonstrated by the relative reactivities of the protonated species in both the bis(ethylenediamine) and bis(trimethylenediamine) complexes

$$P1 > P2 < P3 < P4$$

In general, the bis(trimethylenediamine) species hydrolyses more rapidly than the bis(ethylenediamine) species. The P1 and P2 species react about ten times faster while the P3 species reacts 160 times faster. Protonation can enhance or inhibit different labilising effects and its net effect depends on the relative contributions of these factors. In the base hydrolysis of $Cotn_2(OH)PO_4^-$ and $Coen_2(OH)PO_4^-$, the former species hydrolyses 70 times faster than the latter for the uncatalysed path and 30 times faster for the base catalysed path. The differences in the two systems appear to be solely due to the differences in activation parameters as discussed. It is suggested that steric crowding increases the rates of acid and base hydrolysis significantly.

CHAPTER 6

PRELIMINARY INVESTIGATIONS OF THE DIAQUO-BIS (TRIMETHYLENEDIAMINE) COBALT (III) SYSTEM

6.1 Introduction

It had been hoped, with the isolation of the cis- and trans- diaquo species of the Co(III) bis(trimethylenediamine) system, that a study of the anation reaction between the diaquo species and the phosphate anion may be made. Bjerrum and Rasmussen[48], and Tong and Yankwich[49] have successfully isolated the cis- and trans- isomers of the $(Coen_2(H_2O)_2)^{3+}$ species. They have investigated the acid-base and cis-trans equilibria of this system which facilitated the interpretation of the kinetic data obtained in the anation of $(Coen_2(H_2O)_2)^{3+}$ by PO_4^{3-} anion. Up-to-date no work has been reported on the acid-base and cis-trans equilibria for the $(Cotn_2(H_2O)_2)^{3+}$ species.

6.2 Attempted Isolation of $(Cotn_2(H_2O)_2)^{3+}$ species

The carbonato complex, $(Cotn_2CO_3)\ ClO_4$ was prepared in view of isolating the cis-diaquo species. In acid solution, the carbonate group hydrolyses to liberate carbon dioxide. Since the carbonate group is acting as a bidentate in the complex, the diaquo complex resulting should be initially cis in configuration. It has been found that in the bis(ethylenediamine) system, the diaquo species exists greater than 98% in the cis- form in acid solution[48]. It is not unreasonable to assume that the cis-trans equilibrium for the bis(trimethylenediamine) at low pH to be very similar.

After vacuum drying the solution formed by treating $(Cotn_2CO_3)ClO_3$ with a slight excess of two equivalents of perchloric acid for a week, crystals of cis- $Cotn_2(H_2O)_2(ClO_4)_3$ were obtained. Due to the high solubility of the complex, recrystallisation to obtain a pure product was difficult to achieve. Various methods used to prepare the trans- $(Coen_2(H_2O)_2)^{3+}$ species were adapted to isolate the corresponding trans- $(Cotn_2(H_2O)_2)^{3+}$ species. These involved the reaction of trans- $(Cotn_2Cl_2)^{+}$ salt with Ag_2O [48 49] or $AgClO_4$ [50], but in each case, no crystalline product was isolated.

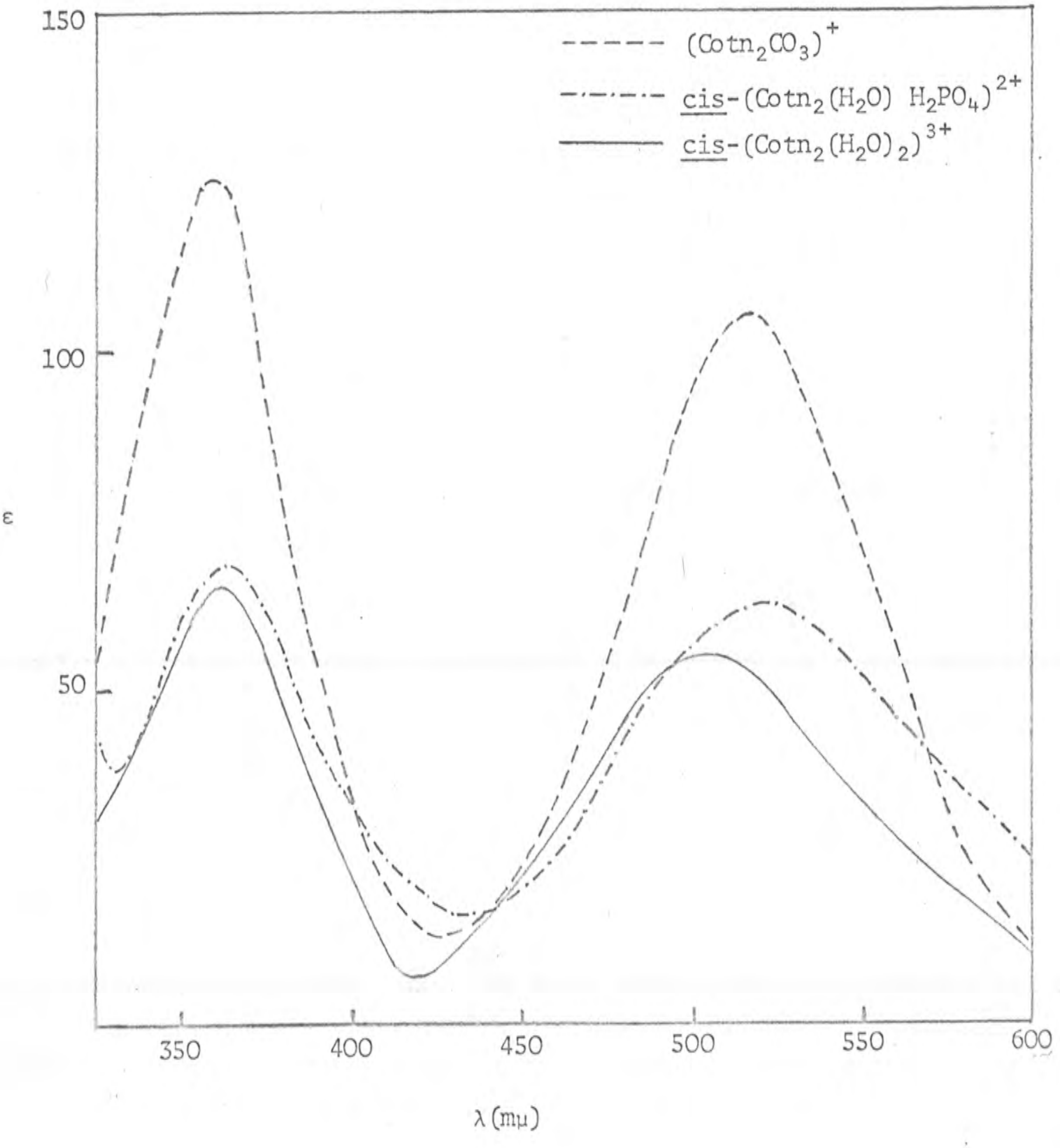
However, assuming that the $(Cotn_2(H_2O)_2)^{3+}$ exists solely as the cis- isomer in low pH, a solution of cis- $(Cotn_2(H_2O)_2)^{3+}$ may be prepared by hydrolysing the $(Cotn_2CO_3)$ ClO_4 complex in perchloric acid. The UV-visible absorption spectrum of the cis- $(Cotn_2(H_2O)_2)^{3+}$ species is shown in Fig. 6.1 exhibiting maxima at 360mμ ($\varepsilon = 65$) and 503mμ ($\varepsilon = 54$). The corresponding cis- $(Coen_2(H_2O)_2)^{3+}$ species exhibits maxima at 359mμ ($\varepsilon = 63.1$) and 492mμ ($\varepsilon = 80.9$).[31]

6.3 Equilibration of $(Cotn_2(H_2O)_2)^{3+}$

Solutions of $(Cotn_2(H_2O)_2)^{3+}$ of varying pH's between 2 and 10 were adjusted to ionic strength of unity with sodium perchlorate (Section 7.4 Chapter 7) and equilibrated at $50.0 \pm 0.1^{\circ}C$ for 14 hours. 5-ml. samples of these solutions were pipetted into 10ml. volumetric flasks cooled in an ice-bath and made up to the

FIG. 6.1

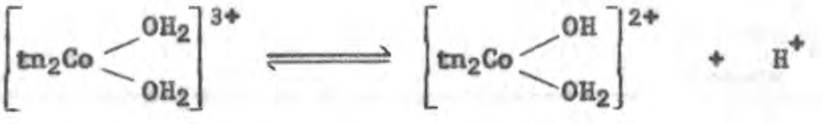
UV-VISIBLE SPECTRA OF BIS(TRIMETHYLENEDIAMINE) COBALT (III) COMPLEX IONS



mark with ice-cold 0.5M perchloric acid. The UV-visible spectra of each solution was then run in 2cm. spectrophotometer cells employing the Unicam SP 800B spectrophotometer. At pH 2 and 2.5 the spectra are identical, giving two peaks at 360mμ (ε = 65) and 503mμ (ε = 54). Thus at these pH values, there seems to be negligible formation of a possible trans- isomer. It was found that at pH's equal to and greater than 3.0, a decomposition product, hydrated cobalt oxide, was formed quite rapidly. On running the spectra of the filtered solutions, it was observed that the peak at longer wavelength, 503mμ, remained in the same position but that at shorter wavelength was masked by what presumably was a strong absorption or light scattering due to the decomposition product. However, the ε-values at 503mμ decreased initially to a minimum value at about pH 6 and increased again with increasing pH.

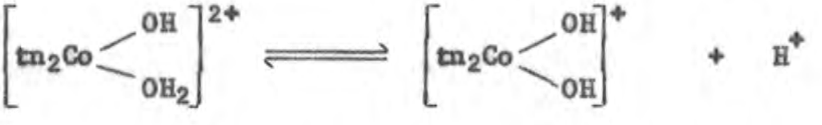
Depending on the pH of the solution the following equilibria would exist.

E.6.1



$$\left[tn_2Co\begin{matrix}OH_2\\OH_2\end{matrix}\right]^{3+} \rightleftharpoons \left[tn_2Co\begin{matrix}OH\\OH_2\end{matrix}\right]^{2+} + H^+$$

E.6.2



$$\left[tn_2Co\begin{matrix}OH\\OH_2\end{matrix}\right]^{2+} \rightleftharpoons \left[tn_2Co\begin{matrix}OH\\OH\end{matrix}\right]^{+} + H^+$$

On examining the effects of having two trimethylenediamine groups instead of two ethylenediamine groups on the acidity constants of the phosphato complexes, the general trend seems to be an increase in acidity with the trimethylenediamine ligands. Hence, it may be expected that the effects of different diamine groups on the acidities of the diaquo complexes to be similar. At pH < 3, the $(Cotn_2(H_2O)_2)^{3+}$ species will be predominant. Between pH 3 to about pH 8 the $(Cotn_2(OH)(OH_2))^{2+}$ species will predominate whereas at higher pH's the main species will be $(Cotn_2(OH)_2)^+$. From the equilibration studies, decomposition appears to be greatest between pH 3 and pH 8. This may be an indication that the $Cotn_2(OH)(OH_2)^{2+}$ species is the most unstable species in aqueous solution.

A solution of $(Cotn_2(H_2O)_2)^{2+}$ was adjusted to pH 7.09 and $\mu = 1$. It is found that at 50°C decomposition occurs in less than five minutes as detected by the continual change in spectrum with time. Also at room temperature decomposition ensues at a slower rate (∿ 5 times slower). Consequently, it is not feasible to follow the much slower anation of the diaquo species by phosphate at this pH which has been shown earlier to be in the region where maximum coordination of the phosphate ligand occurs. This is also the pH where the complex exists solely as the bidentate species.

It is found, by adding phosphate ions to a solution of the diaquo complex at pH 2.5 in the $\frac{(\text{phosphate})}{(\text{diaquo})}$ concentration ratio of 10, there is a spectral change where both the maxima are shifted to longer wavelengths from 360mμ and 503mμ to 367mμ and 520mμ. The final spectrum corresponds to that of cis- $(Cotn_2(H_2O)H_2PO_4)^{2+}$ (see Fig. 6.1). The percentage of the bidentate complex at pH 2.5 is almost negligible for a 1:1 phosphate - diaquo mixture. Evidently the increased phosphate concentration establishes a finite equilibrium concentration of the trimethylenediamine phosphato complex.

However, since the decomposition of the diaquo species is much faster than phosphate substitution at higher pH values, it proved impossible to follow the anation reaction over a wide pH range, as originally planned.

CHAPTER 7

EXPERIMENTAL TECHNIQUES

The experimental methods employed in obtaining the data discussed in this work are described in the following sections.

7.1 Infra-red Spectra

The infra-red spectra of the complex ions were determined in KBr discs using a Perkin Elmer Model 21 double beam infra-red spectrophotometer. The total wavelength scanned was 650 - 4000 cm^{-1}. Since the phosphate bands appear only in the region 800 - 1200 cm^{-1} only this section of the spectrum is illustrated in Chapter 3 Fig. 3.2.

7.2 P.M.R. Spectrum

The P.M.R. Spectrum of the complex ion was measured with a Varian A-60. The sample (0.1M in complex) was prepared in 0.25M H_2SO_4/99.9% D_2O at $2^\circ C$.

7.3 UV-visible Spectra

All UV-visible spectral measurements were made in the thermostated cell block (within the temperature range of $5^\circ C$ to $25^\circ C$) of a Shimadzu QR-50 or a Unicam SP800B spectrophotometer. 1-cm silica cells were used.

7.3.1 Determination of spectra of complex ions

The spectral measurements of aqueous solutions of complex ions were made within the wavelength of 350mμ to 600mμ. All measurements were made against a water blank. Solutions were prepared by weighing the solute into volumetric flasks. All spectra were measured at constant temperature, and within the optical density range of 0.3 to 0.6 to obtain the greatest degree of accuracy.[4]

7.3.2 Ring opening experiments in pH range 3 to 5

Solutions (0.1M) of sodium dihydrogen phosphate and disodium hydrogen phosphate were prepared. The phosphate buffer solutions in pH range 3 to 4 and 4.5 to 5 were prepared by adjusting the pH of the solutions of $NaH_2PO_4.2H_2O$ and Na_2HPO_4 respectively with perchloric acid using a Philips direct reading pH meter.

The $Cotn_2PO_4$ complex (0.0156g.) was weighed into clean, dry volumetric flasks (10ml.). The appropriate buffer solution and another flask containing the complex were both thermostated at 20.3 ± 0.1°C. The reaction was started by dissolving the weighed complex in the buffer solution and making up to the mark in the 10ml. volumetric flask. A 1-cm spectrophotometer cell was quickly filled and placed in the thermostated cell compartment of the Shimadzu QR-50 spectrophotometer. The first optical density reading was taken after 20 seconds and the optical densities were measured at regular time intervals. Finally the infinite time value of the optical density was recorded. The wavelength 540mμ was chosen to follow the reaction since there is a 60% change in optical density in going from the bidentate to the monodentate species.

7.3.3 Ring opening experiments in 0.01M to 2.5M $HClO_4$

Solutions of complex (0.0292M) were prepared.

Stock solutions of perchloric acid (7.38M) and sodium perchlorate (3.75M) were also made up. Twenty-five ml. solutions of acid concentrations within the range of 0.01M to 3.0M were prepared,and adjusted to ionic strength of 3 using sodium perchlorate, by mixing the calculated volumes of the stock solutions.

These solutions of different acid concentrations and the complex solution were thermostated in a water bath at $10.00 \pm 0.05^{\circ}C$. 2.5ml. of the appropriate acid solution were pipetted into a 1-cm spectrophotometer cell and the cell was placed in the thermostated cell block in the Unicam SP800B Spectrophotometer. 0.5ml. of the complex solution was pipetted and injected rapidly into the cell using an attached syringe to ensure rapid and complete mixing. This was necessary since some reaction half times were as short as 3 seconds. The ring opening reaction was followed by the change in optical density at 550mμ and 540mμ for $Coen_2PO_4$ and $Cotn_2PO_4$ complexes respectively.

7.4 Titrimetric methods

7.4.1 Determination of acid dissociation constants of the phosphato cobalt (III) complex ions

A solution of complex (0.0269M) was prepared. Standardised perchloric acid was diluted to 0.0236M. A stock sodium perchlorate solution (0.4M) was made up by dissolving anhydrous sodium perchlorate in distilled water. Sodium hydroxide solution (0.423M) was also prepared and standardised with perchloric acid. All solutions were made up with CO_2 - free water.

The bidentate complex and sodium perchlorate solutions were thermostated at $5^{\circ}C$. A mixture of complex solution (5ml.) and sodium perchlorate solution (10ml.), made up to 25ml. with CO_2 - free water, was prepared in the thermostated Radiometer titration vessel at $5^{\circ}C$. The Radiometer pH meter 25 with Titrator II was operated manually. The titration was carried out quickly (within 15 minutes) with 0.118M $HClO_4$, so that the complex remained solely as the bidentate complex. Ring opening of the complex occurs very slowly at $5^{\circ}C$ ($t_{\frac{1}{2}} \sim 1$ hr.).

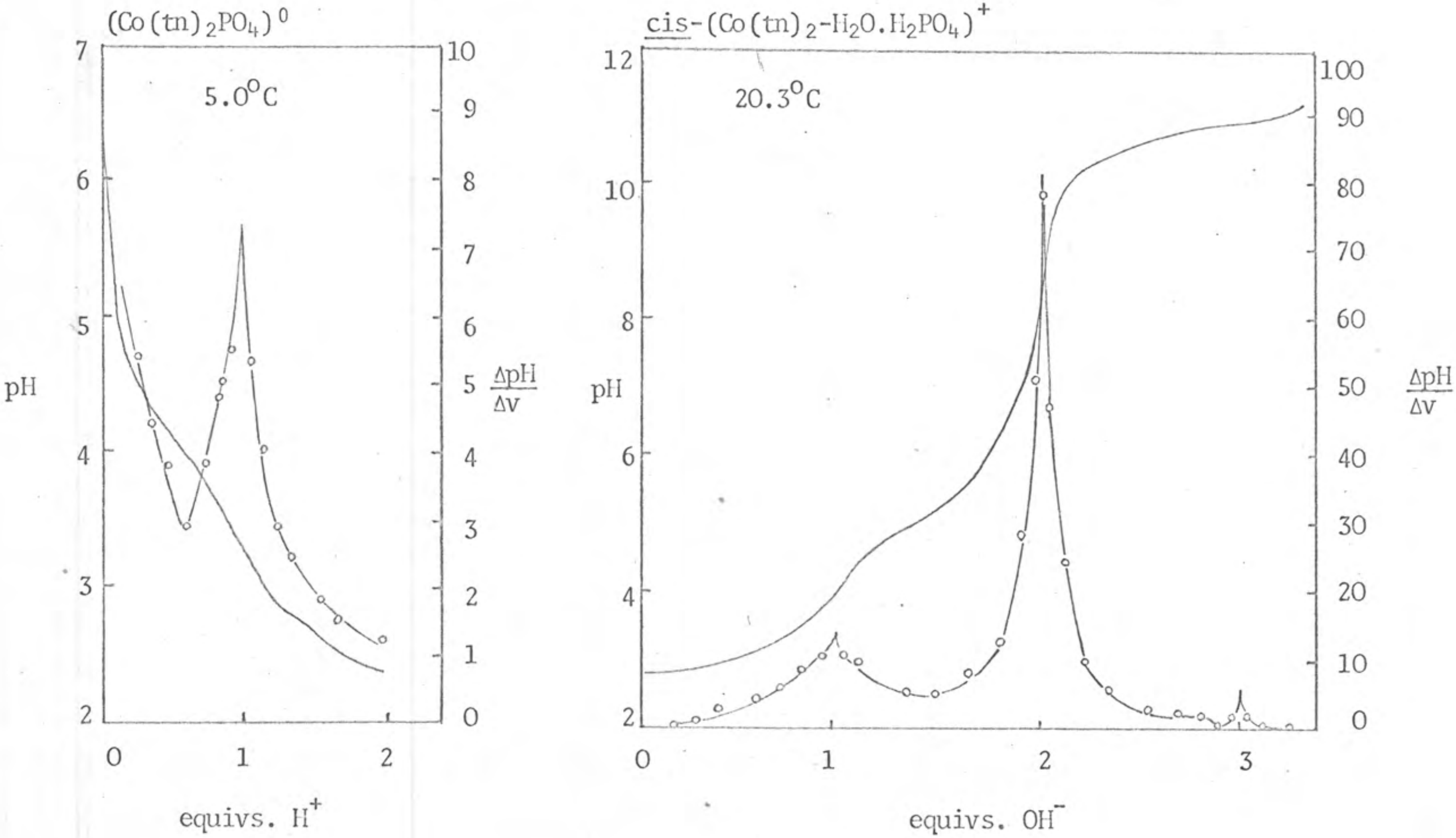
The values of pH and $\frac{\Delta pH}{\Delta v}$ were plotted against v, the volume of titrant added as shown in Fig. 7.1. Since, to a very good approximation,

$$pH = pK_a + \log \frac{(salt)}{(acid)}$$

the pK_a value will be equal to the pH value when half the equivalent of the titrant is added.

FIG. 7.1

TITRATION CURVES AT $\mu = 0.16$



$(Co(tn)_2PO_4)^0$

$\underline{cis}$-$(Co(tn)_2\text{-}H_2O.H_2PO_4)^+$

The pK_a values for the monodentate complex was determined as follows:

A mixture of the bidentate complex solution (5ml.), perchloric acid (10ml.) and sodium perchlorate solution (10ml.) was equilibrated for 20 minutes at room temperature to allow the bidentate ring to open to form the monodentate phosphato complex. The solution was stirred and thermostated at 20.3°C in the jacketed vessel and titrated with standard sodium hydroxide (0.423M).

To obtain the pK_a values at 5°C, the above mixture was prepared at room temperature and allowed to stand for ring opening to occur and then thermostated and titrated at 5°C.

7.5 Kinetic measurements using phosphorus-32 labelled phosphate

7.5.1 Acid Hydrolysis

Perchloric acid solutions in the range 10^{-3}M to 10.6M were prepared by dilution of a standardised analar reagent perchloric acid.

The P^{32} labelled complex (1.6mg) and sufficient inactive complex, to make a 0.0012M solution (10^{-4}M complex for the low acid concentrations), were weighed into a dry 25ml. volumetric flask. The appropriate perchloric acid solution and the flask containing complex were thermostated at 46.3 ± 0.2°C. A stop-clock was started when the reaction was initiated by dissolving the complex in the acid solution and making up to the mark. 1-ml. samples were then pipetted at regular time intervals and quenched in ice-cold 2M perchloric acid (1 to 2ml.) solution at the top of a Zeokarb 225 Cation exchange column. (Column height 5-6cm., diameter 1cm.) The column was washed with distilled water and the free anionic phosphate collected in a 25ml. volumetric flask. The effluent was made up to the 25ml. mark and assayed for P^{32} in a standard skirted wall GM tube with associated counting circuitry. The total count rate was determined by making an aliquot up to 25ml. without separation.

7.5.2 Base Hydrolysis

Sodium hydroxide solutions between 10^{-3}M to 0.3M were prepared. The total ionic strength of the solutions was adjusted to unity by adding the required amount of sodium perchlorate salt.

The reaction was followed by the same procedure as described for acid hydrolysis (Section 7.5.1). The complex concentration was 6×10^{-4}M.

7.5.3 Equilibrium Measurements

A standard solution of P^{32} labelled complex (0.0021M) was prepared. 5ml. aliquots were taken and made up to 25ml. with distilled water and adjusted to a given pH with NaOH or $HClO_4$ within the range $1 < pH < 13$. These solutions were separated by the same procedure described in Section 7.5.1. Equilibrium measurements were made at various times and equilibrium was found to be reached after 3 days. Final pH measurements at 46.3°C were made with the Philips pH meter.

7.6 O^{18} - Measurements

7.6.1 Bond Cleavage Studies

$Cotn_2PO_4$ (0.026g.) was weighed into a clean dry 5ml. volumetric flask and made up to the mark with 2M perchloric acid. 1-ml. of 1.57% O^{18}-enriched water (Yeda Research and Development Co.) was pipetted into the flask. The solution was mixed and thermostated at 56°C. After the hydrolysis was complete, the liberated phosphate was separated by the ion-exchange technique described in Section 7.5.1 for $P^{32}O_4$ assay. To the eluate, a saturated ammoniacal solution of barium nitrate was added to precipitate the phosphate as barium phosphate. The fine white pricipitate was centrifuged and washed twice with water and then with acetone and dried in vacuo and finally heated for ten minutes at 100°C to remove the last traces of solvent.

There is negligible isotopic exchange between phosphate and solvent water[64] under the conditions of this trace experiment so that direct O^{18}-analysis of released phosphate serves as a direct measure of positions of bond cleavage. The O^{18}-content in the barium phosphate was determined by heating with guanidine hydrochloride.[62]

Finely ground guanidine hydrochloride was dried in an oven at 110°C for 30 minutes. The barium phosphate (10mg) and dried guanidine hydrochloride (100mg) were ground together and transferred into the bottom of a break seal tube which was then attached to a vacuum line and evacuated to a pressure of less than 10^{-3}mm of Hg and sealed off. The sealed tube was then heated in a furnace at 400°C overnight. The carbon dioxide was analysed with Hitashi-Perkin Elmer Mass Spectrometer at M/e ratios of 44, 45, 46. Due to the limitations of the instrument, the mass ratio of 46/45 was measured and the mass ratio of 46/44 was determined using the known mass 45/44 ratio of 1.187×10^{-2} (due to $C^{13}O_2{}^{16}$, 1.107% and $C^{12}O^{17}O^{16}$, 0.080%).

7.7 Equilibration Experiments of the Diaquo-bis (trimethylenediamine) cobalt (III) ion in pH range 2 to 11

A stock solution of the diaquo complex (0.1M) was prepared by hydrolysing the carbonato-bis (trimethylenediamine) cobalt (III) perchlorate in perchloric acid, boiling gently to drive off carbon dioxide and making up the solution with carbon dioxide-free distilled water. A stock solution of sodium perchlorate (4M) was also prepared using CO_2-free water. 10ml. of the diaquo solution were pipetted into a 100ml. beaker and 60ml. of CO_2-free water were added. The solution was adjusted to the appropriate pH using perchloric acid and sodium hydroxide solutions and adjusted to ionic strength of unity with the calculated volume of the stock sodium perchlorate solution and made up to 100ml. These solutions were equilibrated at 50.0 ± 0.1°C for 14 hours. Final pH measurements were made after equilibration.

7.8 Standardisation of $HClO_4$ and NaOH

Perchloric acid was standardised against HgO in the presence of excess Kl using methyl red as indicator[63]. Sodium hydroxide was standardised against standard $HClO_4$ using methyl red as indicator.

REFERENCES

1) Taube, H., Chem. Rev. 50, 69 (1952).

2) Ingold, C.K., Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, (1953) Chapters 5 and 7.

3) Basolo, F., Pearson, R.G., Mechanisms of Inorganic Reactions, Wiley (1958) Pg 97.

4) Stranks, D.R., Modern Coordination Chemistry, Interscience Lewis and Wilkins, eds. New York (1960).

5) Langford, C.H., Gray, H.B., Ligand Substitution Processes. Benjamin, New York (1965).

6) Pearson, R.G., Boston, C.R., Basolo, F., J. Am. Chem. Soc., 75, 3089 (1953).

7) Pearson, R.G., Meeker, R.E., Basolo, F., J. Am. Chem. Soc., 78, 2673 (1956).

8) Stranks, D.R., Trans. Far. Soc. 48, 911 (1952).

9) Harris, G.M., Stranks, D.R., Trans. Far. Soc. 48, 137 (1952).

10) Holden, J.S., Harris, G.M., J. Am. Chem. Soc. 77, 1934 (1955).

11) Boyle, J.E., Harris, G.M., J. Am. Chem. Soc. 80, 782 (1958).

12) Lamb, A.B., Mysels, K.J., J. Am. Chem. Soc. 67, 468 (1945).

13) Hunt, J.P., Rutenberg, A.C., Taube, H., J. Am. Chem. Soc. 74, 268 (1952).

14) Bunton, C.A., Llewellyn, D.R., J. Chem. Soc. 1692 (1953).

15) Posey, F.A., Taube, H., J. Am. Chem. Soc. 75, 4099 (1953).

16) Stranks, D.R., Wilkins, R.G., Chem. Reviews 57, 743 (1955).

17) Stranks, D.R., Harris, G.M., J. Chem. Phys. 19, 257 (1951).

18) Stranks, D.R., Harris, G.M., J. Phys. Chem. 56, 906 (1952).

19) Stranks, D.R., Trans. Far. Soc. 51, 505 (1955).

20) Yankwich, P.E., McNamara, J.E., J. Chem. Phys. 20, 1325 (1952).

21) Soito, E., Lazard, B., J. Inorg. Nucl. Chem. 1, 218 (1955).

22) Posey, F.A., Taube, H., J. Am. Chem. Soc. 79, 255 (1957).

23) Andrade, C., Taube, H., Inorg. Chem. 5, 1087 (1966).

24) Barraclough, C.G., Murray, R.S., J. Chem. Soc. 7047 (1965).

25) Duff, J., J. Chem. Soc. 123, 560 (1923).

26) Duval, R., Duval, C., Compt. rend. 189, 573 (1929).

27) Klement, R., Z. anorg. allgem. Chem., 156, 237 (1926).

28) Von Siebert, H., Z. anorg. allgem. Chem., 296, 280 (1958).

29) Schmidt, N., Taube, H., Inorg. Chem. 2, 698 (1963).

30) Lincoln, S.F., Ph.D. thesis (1966).

31) Lincoln, S.F., Stranks, D.R., Aust. J. Chem. (in press)

32) Lincoln, S.F., Stranks, D.R., Aust. J. Chem. (in press)

33) Lincoln, S.F., Stranks, D.R., Aust. J. Chem. (in press)

34) Lincoln, S.F., Stranks, D.R., Aust. J. Chem. (in press)

35) Lincoln, S.F., Stranks, D.R., Aust. J. Chem. (in press)

36) Barraclough, C.G., Tobe, M.L., J. Chem. Soc. 1993 (1961).

37) Staples, P.J., J. Chem. Soc. 745 (1964).

38) Staples, P.J., J. Chem. Soc. 7320 (1965).

39) Staples, P.J., J. Chem. Soc. (A) 986 (1966).

40) Lambert, D.G., Mason, J.G., J. Am. Chem. Soc. 88, 1633 (1966).

41) Lambert, D.G., Mason, J.G., J. Am. Chem. Soc. 88, 1637 (1966).

42) Murray, R.S., Ph.D. thesis (1967).

43) Martell, A.E., Calvin, M., Chemistry of the Metal Chelate Compounds, Prentice-Hall, New York, 1952, Pg. 137.

44) Bailar, Jr. J.C., Work, J.B., J. Am. Chem. Soc. 68, 233 (1946).

45) Von Linhard, M., Stim, G., Z. anorg. Chem., 268, 105 (1952).

46) Inorganic Synthesis Vol. II Pg. 222.

47) Bauer, H.F., Drinkard, W.C., J. Am. Chem. Soc. 82, 5031 (1960).

48) Bjerrum, J., Rasmussen, S.E., Acta. Chem. Scand. 6, 1265 (1952).

49) Tong, J.Y., Yankwich, P.E., J. Am. Chem. Soc. 80, 2664 (1958).

50) Kruse, W., Taube, H, J. Am. Chem. Soc. 83, 1280 (1961).

51) Mori, M., Shibata, M., Kyuno, E., Adachi, T., Bull. Chem. Soc. Japan, 29 883 (1956).

52) Mori, M., Shibata, M., Kyuno, E., Hoshiyama, K., Bull. Chem. Soc. Japan, 31 291 (1958).

53) Searle, G.H., Ph.D. thesis (1963).

54) Vogel, A.I., Quant. Inorg. Anal., Longmans, London, Pg. 614 (1961).

55) Nakamoto, K., "Infra-Red Spectra of Inorganic and Coordination Compounds", Wiley, New York Pg 107 (1963).

56) Gill, N.S., Nuttall, R.H., Scaife, D.E., Sharp, D.W.A., J. Inorg. Nucl. Chem., 18, 79 (1961).

57) Herzberg, G., Infra-red and Raman Spectra of Polyatomic Molecules, Van Nostrand, New York, Pg 167 (1945).

58) Buckingham, D.A., Durham, L., Sargeson, A.M., Aust. J. Chem. 20, 257 (1967).

59) Jolly, W.L., Harris, A.D., Briggs, T.S., Inorg. Chem. 4, 1064 (1965).

60) Bronsted, J.N., Z. phys. chem. 122, 383 (1926).

61) Bunnet, J.F., J. Am. Chem. Soc., 83 4966 (1961).

62) Boyer, P.D., Graves, D.J., Suelter, C.H., Dempsey, M.E., Anal. Chem. 33 1906 (1961).

63) Vogel, A.I., Quant. Inorg. Anal., Longmans, London, Pg 244 (1961).

64) Bunton, C.A., Llewellyn, D.R., Vernon, C.A., and Welch, V.A., J. Chem. Soc. 3293 (1960).

65) Huckital, D.H., Taube, H., Inorg. Chem. 4 1660 (1965).

66) Stranks, D.R., Modern Coordination Chemistry, Interscience Lewis and Wilkins, eds. New York (1960) Pg 100.