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ACID-CATALYSED REACTIONS OF TRANSITION METAL COMPLEXES

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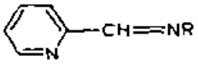
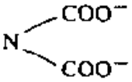
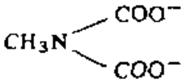
CONTENTS

ABBREVIATIONS

en	1, 2-diaminoethane (ethylenediamine)
dien	2, 2'-diaminodiethylamine (diethylenetriamine)
tren	tri-(2-aminoethyl)amine
trien	*N*, *N'*-di-(2-aminoethyl)-ethylenediamine (triethylenetetramine)
penten	*N*, *N*, *N'*, *N'*-tetra-(2-aminoethyl)ethylenediamine
pn	$NH_2CH_2\underset{CH_3}{C}HNH_2$ 1, 2-diaminopropane (propylenediamine)
tn	$NH_2CH_2CH_2CH_2NH_2$ 1, 3-diaminopropane (trimethylenediamine)
N-pren	$NH_2CH_2CH_2NHCH_2CH_2CH_3$
ptn	1, 2, 3-triaminopropane
dapa	2, 2'-diaminodipropylamine
cyclam	1, 4, 8, 11-tetraazacyclotetradecane
teta	5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane (isomer (a))
tetb	isomer (b)
dipy	2, 2'-dipyridyl
phen	1, 10-phenanthroline
RPI	pyridinalalkylimine (R = alkyl),
	
IDA	iminodiacetate ion,  $HN\begin{smallmatrix}COO^-\\COO^-\end{smallmatrix}$
MIDA	methyliminodiacetate ion,  $CH_3N\begin{smallmatrix}COO^-\\COO^-\end{smallmatrix}$
H_4Y	ethylenediaminetetraacetic acid
EDTA	Y^{4-}

A. INTRODUCTION

That the hydrogen ion concentration may have a marked effect on the rate, mechanism and nature of reaction products is well known. Examples of acid-catalysed reactions of organic compounds are legion. In this review the reactions of transition metal complexes which may be influenced by the hydrogen ion concentration are discussed. The kinetic and mechanistic aspects are surveyed along with relevant preparative and physicochemical work. Evidence for the existence of protonated species is examined.

Many of the reactions discussed here are hydrolysis reactions. Hydrolyses may be classified into three types, viz. basic hydrolysis, aquation (often referred to as acid hydrolysis) and acid-catalysed hydrolysis. Some transition metal complexes may exhibit all three types of behaviour; e.g. the cation[1] *trans*-$[Co(en)_2F_2]^+$.

(1) Basic hydrolysis, the overall reaction being replacement of a fluoro group by a hydroxide ion

$$trans\text{-}[Co(en)_2F_2]^+ + OH^- \rightarrow [Co(en)_2F(OH)]^+ + F^- \qquad (1)$$

These reactions are usually studied using solutions of pH 10–13.

(2) Aquation, the replacement of, for example, a fluoro group, by water

$$trans\text{-}[Co(en)_2F_2]^+ + H_2O \rightarrow trans\text{-}[Co(en)_2F(H_2O)]^{2+} + F^- \tag{2}$$

The aquation reaction is usually studied using solutions of pH $\leqslant 4$. Above pH 4 the basic hydrolysis reaction may become significant and interfere.

(3) Acid-catalysed aquation, the removal of fluoro ligand being catalysed by acid. The final product is the aquo complex.

$$trans\text{-}[Co(en)_2F_2]^+ + H_3O^+ \longrightarrow [Co(en)_2F(H_2O)]^{2+} + HF \tag{3}$$

The acid concentration at which reaction (3) becomes significant, compared, say, with the aquation reaction, will vary from one substrate to another.

Equations (1), (2) and (3) describe overall reactions; they say nothing about mechanism. In this review we will be concerned only with reactions of type (3).

Acid-catalysed reactions occur, or are feasible, for complexes which contain a basic ligand (i.e. one which is easily protonated, or easily forms hydrogen bonds, or one which is the anion of a weak acid). The criteria given in brackets are, in fact, a restatement of the basicity requirement. Some ligands which fulfil these criteria and whose complexes take part in acid-catalysed reactions are: F^-, NO_2^-, ONO^-, N_3^-, CN^-, CO_3^{2-}, acetate and some chelate ligands. The reactions will be discussed in terms of the stereochemistry of the substrate (e.g. octahedral or square planar) and may be classified further according to the particular ligand being replaced. The acid-catalysed reactions of chelate complexes involve special features, e.g. the presence of more than one metal–ligand bond, ring strain and special conformational or stereochemical requirements, all of which may have a profound influence on rate and mechanism. For these reasons the reactions of chelate-complexes are discussed in a separate section.

The reactions of carbonato and oxalato complexes are, however, discussed in the first section because the carbonato ligand may act as a monodentate as well as a bidentate ligand. Furthermore most of the proposed mechanisms involve monodentate bicarbonato— or acid—oxalato species.

B. OCTAHEDRAL COMPLEXES

(i) Fluoro complexes

One of the earliest reports of acid-catalysed aquation was that of *trans*-$[Co(en)_2F_2]^+$ ion[1]. The rate of reaction is first order in the concentration of complex ion and the corresponding pseudo-first-order rate constant may be expressed as

$$k_{obs} = k_1 + k_2'[H^+] \tag{4}$$

Basolo et al. classify this as an S_E2 reaction on the basis of the following mechanism.

$$(\mathrm{en})_2\mathrm{FCoF}^+ + \mathrm{H_2O} \xrightarrow[\text{slow}]{k_1} (\mathrm{en})_2\mathrm{FCoOH_2}^{2+} + \mathrm{F}^- \text{ (aquation)}$$

$$(\mathrm{en})_2\mathrm{FCoF}^+ + \mathrm{H}^+ \xrightleftharpoons{\text{instantaneous}} (\mathrm{en})_2\mathrm{FCoFH}^{2+}; (K_{\mathrm{eq}})$$

$$(\mathrm{en})_2\mathrm{FCoFH}^{2+} + \mathrm{H_2O} \longrightarrow (\mathrm{en})_2\mathrm{FCoOH_2}^{2+} + \mathrm{HF}$$

Scheme 1.

Hence,

$$\text{Rate} = (k_1 + k_2K_{\mathrm{eq}}[\mathrm{H}^+])\ [\text{complex}] \tag{5}$$

and

$$k_{\mathrm{obs}} = k_1 + k_2K_{\mathrm{eq}}[\mathrm{H}^+] \tag{6}$$

However, an alternative nomenclature has been used. A bimolecular reaction, illustrated above, has been designated S_N2CA (where CA denotes conjugate acid of the substrate, i.e. the protonated substrate). This takes account of the fact that in scheme 1 the rate-determining step is bimolecular and is a nucleophilic attack by water on the conjugate acid (CA). Furthermore, although the proton may be regarded as an electrophilic reagent the rate-determining step is not the protonation but either (1) slow loss of HF followed by fast attack by a water molecule (S_N1CA) or, less likely, (2) slow attack by a water molecule followed by rapid loss of an HF molecule (S_N2CA). Basolo et al. used aqueous nitric acid as solvent and a plot of log k_{obs} vs. log[$\mathrm{HNO_3}$] is a straight line of approximately unit slope.

The hydrolysis of $[\mathrm{Co(NH_3)_5F}]^{2+}$ ion is acid-catalysed[2] in solutions of nitric acid—sodium nitrate (ionic strength 0.112 *M*). The observed rate constants obey eqn. (6) and the mechanism (scheme 1) was postulated. The hydrolysis of $[\mathrm{Cr(NH_3)_5F}]^{2+}$ is acid-catalysed[3] but the catalysis is much less marked than for the cobalt analogue, being significant only when $[\mathrm{H}^+] > 0.1\ M$. The ion $[\mathrm{Cr(H_2O)_5F}]^{2+}$ exhibits similar behaviour[4] although the background aquation is significant in this case. Scheme 1 was again the proposed mechanism. More recently the hydrolysis of $\mathrm{Co(tren)F_2}^+$ ion in acidic media has been reported[5]. The results were very similar in form to those reported for the other fluoro species.

In some of the above investigations the reactions were also studied using deuterium oxide as solvent. The rate constants are higher for $\mathrm{D_2O}$ as solvent than for analogous protium solutions. This is attributed to a more favourable position of the pre-equilibrium (step K_{eq} of scheme 1) because deutero-acids are weaker acids than their protium analogues.

(ii) Azido complexes

The hydrolysis of *cis*- and *trans*-$[\mathrm{Co(en)_2(N_3)_2}]^+$ ions in perchloric acid—sodium perchlorate solutions, of constant ionic strength, has been studied[6]. At lower acid concentrations ($[\mathrm{H}^+] \leqslant$ ca. 2.5 *M*) a plot of log k_{obs} vs. log $[\mathrm{H}^+]$ is linear with unit slope. At higher acid concentrations, however, this relationship breaks down and the observed rate constant increases sharply with further small increases in the acid concentration. Further experiments[7] using acid solutions without added salts showed that at the lowest acid concentrations, i.e. $[H^+] \leqslant$ ca. 2.0 M, the slope of log k_{obs} versus log $[H^+]$ is ca. 1.4. As the acid concentration is further increased the kinetic behaviour is analogous to that reported for the *trans*-$[Co(en)_2ClN_3]^+$ ion which is described below.

The hydrolysis of *trans*-$[Co(en)_2ClN_3]^+$ ion in different aqueous acids has been reported[8]. The results show the following features (see Fig. 1).

(1) At relatively low acid concentrations there is a steady increase in k_{obs} as $[H^+]$ increases (region A).

(2) In the intermediate acid concentrations there is a sharp inflexion in the rate constant vs. $[H^+]$ profile (region B).

(3) Eventually an acid concentration is reached at which a maximum value of k_{obs} (region C) is reached.

The three regions were interpreted as corresponding to the the following situations: region A – a low degree of protonation of the complex; region B – the complex is appreciably protonated; and region C – the substrate is fully protonated.

The results were analysed quantitatively as follows. A plot of log k_{obs} versus $-H_0$ (where H_0 = Hammett acidity function) is a straight line of unit slope at lower and intermediate acid concentrations. However, the plot gradually deviates from unity as the substrate becomes appreciably or greatly protonated. These results were explained in terms of the following unimolecular mechanism (scheme 2).

$$\underset{(SN_3^{+})}{[Co(en)_2ClN_3]^{+}} + H_3O^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(SN_3H^{2+})}{[Co(en)_2ClN_3H]^{2+}} + H_2O$$

(rapid pre-equilibrium)

$$\underset{(SN_3H^{2+})}{[Co(en)_2ClN_3H]^{2+}} \xrightarrow{k_2\ (slow)} \underset{(S^{2+})}{[Co(en)_2Cl]^{2+}} + HN_3$$

$$[Co(en)_2Cl]^{2+} + H_2O \xrightarrow{(fast)} [Co(en)_2ClH_2O]^{2+}$$

Scheme 2.

$$\text{Rate} = k_2[SN_3H^{2+}] \tag{7}$$

The actual concentration of the intermediate $[SN_3H^{2+}]$ could not be determined directly because the subsequent hydrolysis reactions are quite fast ($t_{\frac{1}{2}}$ is a few minutes at 25°C). However, the rate equation (7) was transformed to a more suitable form by analogy with a Hammett indicator equilibrium, i.e. we may write

$$H_+ = pK_a - \{\log [SN_3H^{2+}]/[SN_3^{+}]\} \tag{8}$$

giving

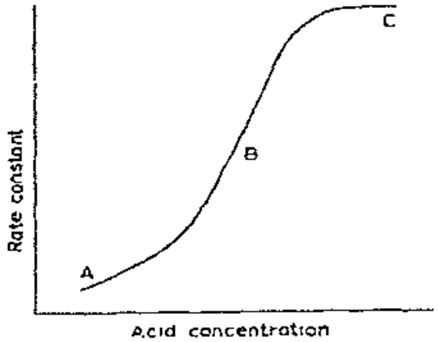


Fig. 1. See text. After ref. 8, by permission of the authors and the Chemical Society, London.

$$\text{Rate} = k_2 \frac{h_+}{h_+ + K_a} [\text{complex}] \qquad (9)$$

where $h_+ = -\text{antilog}\, H_+$ and $[\text{complex}] = [SN_3H^{2+}] + [SN_3{}^+]$.
Two extreme conditions may be considered, viz.

(1) At high acid concentrations $h_+ \gg K_a$. From eqn. (9),

$$\text{Rate} = k_2 [\text{complex}] \qquad (10)$$

i.e. the rate is independent of the acid concentration as observed experimentally.
(2) At low acid concentrations $K_a \gg h_+$, then

$$\text{Rate} = k_2 h_+ \ [\text{complex}]/K_a \qquad (11)$$

i.e. $k_{obs} = k_2 h_+ \ K_a$

or

$$\log k_{obs} = \log k_2 - H_+ + pK_a \qquad (12)$$

Inspection of eqn. (12) shows that if the maximum rate constant k_2 can be measured, then there is only one unknown quantity (K_a). K_a values were determined as follows. An estimated value of K_a was inserted in eqn. (12) and $\log k_{obs}$ was computed for various values of H_0. This gave a hypothetical plot of $\log k_{obs}$ vs. H_0. Several such plots were constructed and the experimental results were plotted. The hypothetical value of K_a was further refined until the experimental and hypothetical curves for $\log k$ vs. H_0 were in good agreement. The value of K_a which gave such a condition was taken as the true K_a value.

The most notable feature of the results (see Table 1) is that the K_a value of a given complex ion differs from acid to acid. This has been confirmed by equilibrium studies[9] for the less labile complex ion $[Rh(NH_3)_5N_3]^{2+}$. In the actual correlations H_0, and not H_+, was used as it is much better documented in the literature. It has been shown, however, for

TABLE 1

Kinetically determined acid dissociation constants for protonated azido complex ions in aqueous acids

Complex	Acid	K_a	Temp.	Ref.
trans-$[Co(en)_2ClN_3]^+$	$HClO_4$	20,000	15.0	8
	H_2SO_4	3,000	25.0	8
cis-$[Co(en)_2(N_3)_2]^+$	H_2SO_4	50	25.0	7
	HCl	70	15.0	7
$[Co(NH_3)_5N_3]^{2+}$	H_2SO_4	600	25.0	11
$[Rh(NH_3)_5N_3]^{2+}$	H_2SO_4	90	60.0	11
	$HClO_4$	190	87.5	10
$[Cr(NH_3)_5N_3]^{2+}$	H_2SO_4	1,800	10.0	11

some ranges of sulphuric acid concentration that H_0 and H_+ are parallel. Therefore, correlations involving the rates of change of H_0 or H_+ with log k_{obs}, i.e. slopes of plots are valid. The K_a values determined using H_0 values contain a consistent systematic error, i.e. the difference between H_0 and H_+. However, comparisons between K_a values determined by the one method are valid and meaningful.

The acid-catalysed hydrolyses of $[M(NH_3)_5N_3]^{2+}$ ions (where M = Cr, Co or Rh) have been studied[10, 11] and the acid dissociation constants of the conjugate acids have been evaluated. The results (see Table 1) show that the K_a value varies somewhat from metal to metal. For a given series of related complexes, however, the main factor which determines the range of pK_a values is the basic group being protonated. At room temperature the rate of hydrolysis of the completely protonated rhodium analogue is slow enough to allow ionisation ratios to be measured (see Section F). The results are in general agreement with those determined kinetically using eqn. (12). Arrhenius parameters for the acid-catalysed hydrolysis of some azido complexes are given in Table 2.

The effect of added anions on the hydrolysis of *trans*-$[Co(en)_2ClN_3]^+$ ion has been reported[12]. Experiments were performed using, as solvents, acids concentrated enough to ensure complete protonation of the substrate. By studying the completely protonated substrate it was possible to avoid errors due to added salts changing the acidity of the medium (it is known that the acidity function of an aqueous acid is altered by the presence of added salts). The rate of hydrolysis of the conjugate acid *trans*-$[Co(en)_2ClN_3H]^{2+}$ in aqueous perchloric acid decreases as small amounts of sulphate or bisulphate ions are added. However, it was not possible to add sufficient alkali metal salt to depress the rate constant to that for aqueous sulphuric acid solvent. The existence and influence of ion-pairs was demonstrated. The existence of other medium effects could not be entirely ruled out.

Holba[13] studied the acid-catalysed aquation of *trans*-$[Cr(en)_2(N_3)_2]^+$ by the colorimetric method using ferric ions to form ferric azide. The observed first-order rate constants were given by eqn. (14). No maximum rate of hydrolysis was reported. The hydrolysis of $[Cr(H_2O)_5N_3]^{2+}$ ion is reported[14] to follow eqn. (13)

$$k_{obs} = k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2} \tag{13}$$

TABLE 2

Arrhenius parameters for the acid-catalysed hydrolysis of azido complexes

Complex	Acid	E (kcal. mole^{-1})	log A	Ref.
$Cr(NH_3)_5N_3^{2+}$	H_2SO_4	19.7	12.6	11
$Rh(NH_3)_5N_3^{2+}$	$HClO_4$	24.6	9.6	10
$Rh(NH_3)_5N_3^{2+}$	H_2SO_4	27.3	14.3	11
$Co(NH_3)_5N_3^{2+}$	H_2SO_4	24.7	14.2	11
$Co(NH_3)_5N_3^{2+}$	$HClO_4$	47.9		10b
trans-$Co(en)_2ClN_3$	H_2SO_4	25.2	16.0	12
trans-$Co(en)_2ClN_3$	HCl	25.2	16.5	12
trans-$Co(en)_2ClN_3$	$HClO_4$	25.2	16.8	12
cis-$Cr(en)_2(N_3)_2$	$HClO_4$	15		13
$Cr(H_2O)_5N_3$	$HClO_4$	23.2[a]		14
cis-$Co(en)_2(N_3)_2$	$HClO_4$	26.7	15.9	23

[a] This figure is the $\Delta H^{\ddagger}$ value.

A detailed study of the acid-catalysed hydrolysis of $[Co(CN)_5N_3]^{3-}$ ion[15] has been made and the results provide some of the best evidence for a unimolecular mechanism. The kinetic results (at 40°, $I = 1.0$) are given by eqn. (14)

$$k_{\text{obs}} = \frac{k_a K[H^+]}{1 + K[H^+]} \tag{14}$$

where K is an *association* constant. In the acid solutions of constant ionic strength, without thiocyanate ions present the reaction products are $[Co(CN)_5H_2O]^{2-}$ and HN_3. Although the presence of 0.40 to 0.90 M thiocyanate ions do not affect the rate of acid-catalysed aquation, $[Co(CN)_5NCS]^{3-}$ becomes an increasingly more important product as the thiocyanate ion concentration increases. Thus the decrease in the formation of $[Co(CN)_5H_2O]^{2-}$ in the presence of thiocyanate ions must be caused by capture of a reactive intermediate. The overall mechanism may then be written

$$Co(CN)_5N_3^{3-} + H^+ \underset{}{\overset{K}{\rightleftharpoons}} Co(CN)_5N_3H^{2-} \tag{15}$$

$$Co(CN)_5N_3H^{2-} \xrightarrow[\text{(rate-determining)}]{k_a} Co(CN)_5^{2-} + HN_3 \tag{16}$$

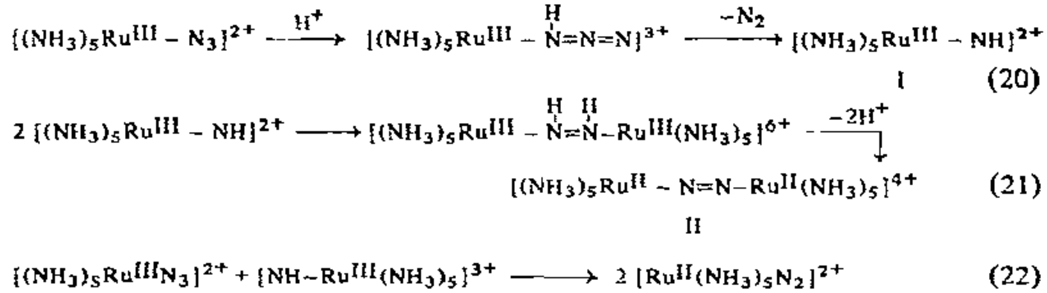
$$Co(CN)_5^{2-} + H_2O \xrightarrow{k_2} Co(CN)_5H_2O^{2-} \tag{17}$$

$$Co(CN)_5^{2-} + NCS^- \xrightarrow{k_3} Co(CN)_5NCS^{3-} \tag{18}$$

Ion-pairing complications were also neatly avoided because association between the anions $[Co(CN)_5H_2O]^{2-}$ and NCS^- should be very small indeed. Azido complexes of ruthenium are unstable in both the solid state and in solution[16], decomposing according to eqn. (19). This reaction occurs with several azidoruthenium(III) complexes, viz. $[Ru(NH_3)_5N_3]^{2+}$, *cis*-$[Ru(en)_2(N_3)_2]^+$, *cis*-$[Ru(en)_2(N_3)N_2]^+$ and $[Ru(EDTA)(N_3)]^{2+}$.

$$Ru(NH_3)_5N_3^{2+} \longrightarrow Ru(NH_3)_5N_2^{2+} + \tfrac{1}{2}N_2 \qquad (19)$$

In acid solution the rates of decomposition increase markedly and the products are more complicated[17,18], i.e. dimeric nitrogen-bridged complexes are formed in addition to monomeric nitrogen species. The mechanism postulated (scheme 3) is cleavage of a N–N bond in the azido ligand, as rate-determining step, releasing nitrogen and yielding a metallated nitrene intermediate I.



$$[(NH_3)_5Ru^{III}-N_3]^{2+} \xrightarrow{H^+} [(NH_3)_5Ru^{III}-\overset{H}{N}{=}N{=}N]^{3+} \xrightarrow{-N_2} \underset{\text{I}}{[(NH_3)_5Ru^{III}-NH]^{2+}} \qquad (20)$$

$$2\,[(NH_3)_5Ru^{III}-NH]^{2+} \longrightarrow [(NH_3)_5Ru^{III}-\overset{H}{N}{=}\overset{H}{N}-Ru^{III}(NH_3)_5]^{6+} \xrightarrow{-2H^+} \underset{\text{II}}{[(NH_3)_5Ru^{II}-N{=}N-Ru^{II}(NH_3)_5]^{4+}} \qquad (21)$$

$$[(NH_3)_5Ru^{III}N_3]^{2+} + [NH-Ru^{III}(NH_3)_5]^{3+} \longrightarrow 2\,[Ru^{II}(NH_3)_5N_2]^{2+} \qquad (22)$$

Scheme 3.

Coordinated azido ligand is a base and is an effective trap for the coordinated nitrene. Thus an attack of nitrene on azido ligand should be favoured at the expense of dimerisation. This is observed; as the initial concentration of complex is increased there is an increase in the contribution from eqn. (22) and a decrease in the formation of the dimer (eqn. (21)). The results of product studies showed (1) the production of large amounts of dimer, (2) the absence of dimer formation unless acid is present and (3) a marked decrease in formation of dimer II as the original concentration of $[Ru(NH_3)_5N_3]^{2+}$ increases. The appearance of the dimer is very rapid and could not have resulted from a reaction between $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5N_2]^{2+}$ because the latter reaction would take several hours[19] under the same experimental conditions.

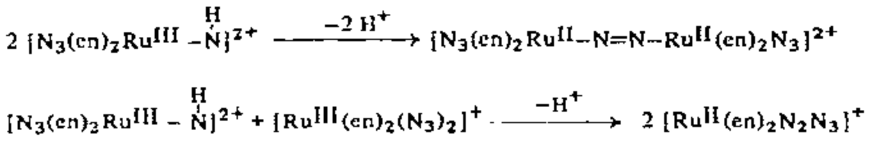
In dilute solutions of complex where dimerisation predominates small amounts of thiourea, diethyl sulphide or iodide ions prevented formation of any dimer. However, the reagents Cl^-, PF_6^- or CH_3CN had no observable effect on the course of the acid-catalysed reaction. This is interpreted in terms of the Lewis acid character of nitrene I which is quenched more rapidly by, for example, iodide ions, than it can dimerise.

The acid-catalysed aquation of *cis*-$[Ru(en)_2(N_3)_2]^+$ ion occurs via a similar series of reactions (scheme 4). In this case a "thiourea trapped" product was isolated and its analysis corresponded to $[Ru(en)_2(H_2O)(N{-}SCN_2H_4)][B(C_6H_5)_4]_3$.

The aquations follow the general rate law

$$k_{obs} = k_0 + k_1[H^+] \qquad (23)$$

The rate of decrease of the original complex is not related exactly to the formation of one particular product. The diazido complex is consumed in several reactions, viz. the formation of metallated nitrene, reaction with metallated nitrene (eqn. (25)), a contribution from the so-called neutral decomposition and acid-catalysed aquation of the coordinated azido ligand. The acid-catalysed aquation becomes more important as the acid concentration increases (at room temperature it accounts for ca. 17% of the reaction in 4.0 *M* sulphuric acid and ca. 29% in 8.5 *M* sulphuric acid).



$$2\,[N_3(en)_2Ru^{III}-\overset{H}{N}]^{2+} \xrightarrow{-2\,H^+} [N_3(en)_2Ru^{II}-N{=}N-Ru^{II}(en)_2N_3]^{2+} \qquad (24)$$

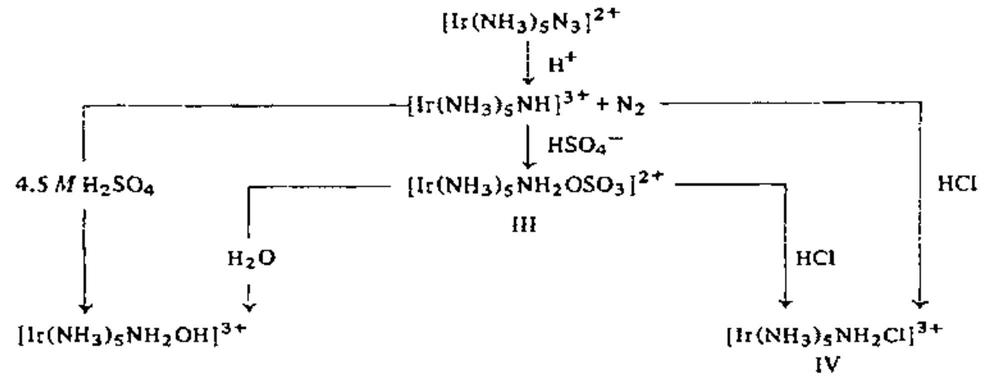
$$[N_3(en)_2Ru^{III}-\overset{H}{N}]^{2+} + [Ru^{III}(en)_2(N_3)_2]^+ \xrightarrow{-H^+} 2\,[Ru^{II}(en)_2N_2N_3]^+ \qquad (25)$$

Scheme 4.

A search was made for similar acid-catalysed reactions in which azido complexes yield nitrogen gas and nitrogen or nitrene complexes. Azido complexes of cobalt(III), rhodium(III), platinum(II), palladium(II) and gold(III) produced no gas when treated with 4 *M* sulphuric acid at room temperature. However, the iridium complex, *trans*-$[Ir(en)_2(N_3)_2]PF_6$ does produce nitrogen[20]. Reaction of acids with $[Ir(NH_3)_5N_3](ClO_4)_2$ yields some interesting compounds[21,22] as shown in scheme 5. When the azido complex is treated with 4.5 *M* sulphuric acid, in the complete absence of chloride ions, and then perchloric acid is added, a white precipitate of $[Ir(NH_3)_5NH_2OH](ClO_4)_3$ is formed. The hydroxylamine complex has a pK_a value and infrared absorption bands characteristic of NH_2OH. If an aqueous solution of $[Ir(NH_3)_5N_3](ClO_4)_2$ is treated with concentrated sulphuric acid there is a vigorous evolution of nitrogen gas and a white solid III is precipitated. If III is treated with barium chloride solution and the barium sulphate filtered off then addition of perchloric acid to the filtrate yields $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ (IV). This white crystalline solid IV undergoes reactions characteristic of chloramine, e.g.

$$[Ir(NH_3)_5NH_2Cl]^{3+} + 2\,I^- + H^+ \longrightarrow [Ir(NH_3)_6]^{3+} + Cl^- + I_2 \qquad (26)$$

Compound IV is air-stable, diamagnetic and stable in aqueous acids.



Scheme 5. Reproduced from refs. 17 and 18 and by permission of the authors and the American Chemical Society.

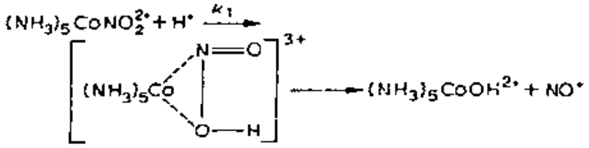
Kinetic studies show that in 4.5 *M* sulphuric acid $[Ir(NH_3)_5N_3]^{2+}$ ion is decomposed rapidly. In sulphuric acid the rate of reaction is a function of h_0. In hydrochloric acid, and in perchloric acid, at the same h_0 value, the rates of reaction are almost identical with the rate in sulphuric acid. That the rate is independent of the anion of the acid shows the absence of nucleophilic assistance in the removal of nitrogen and adds further support for the nitrene intermediate.

The behaviour of the iridium complexes is to be contrasted with that of the ruthenium complexes discussed earlier. The ruthenium(III) azido complexes react to yield nitrenes which in turn give nitrogen complexes of ruthenium(II). The facile reduction of ruthenium(III) to ruthenium(II) makes possible the internal redox reactions which give the observed products. In the case of iridium, however, there are no iridium(II) complexes and it was postulated that the iridium nitrene complexes should, therefore, behave differently from those of ruthenium.

(iii) Nitro complexes

Nitro complexes form probably the most extensively studied group of complexes as far as acid-catalysed reactions are concerned. The hydrolysis of *cis*- and *trans*-$[Co(en)_2(NO_2)_2]^+$ ions in aqueous sodium perchlorate–perchloric acid solutions ($I = 3.50$) has been studied[23]. A plot of log k_{obs} vs. log$[HClO_4]$ is a straight line of unit slope. These results suggest a mechanism in which water is involved in the transition state. However, the hydrolysis of a whole series of complex ions, viz. *cis*- or *trans*-$[Co(en)_2XNO_2]^+$ (where X = NO_2, Cl, NCS or NH_3) in much more concentrated solutions of strong acids, without added salts, was then studied[24, 25]. The observations were analysed by the methods of Hammett and Zucker and of Bunnett and the results favour a mechanism in which water is not involved in the rate-determining step. Such differences in kinetic behaviour, i.e. when the ionic strength is constant k_{obs} depends on log [ACID] but when no added salts are present k_{obs} depends on the acidity function, have been observed in organic chemistry, e.g. the hydrolysis of alkyl sulphites[26]. In the above series the ease of protonation, as estimated by the acid concentration which effects appreciable acid catalysis, is in the order *trans*-NO_2 $\gg$ *cis*-NO_2 $>$ *cis*-$(NCS)NO_2$ $>$ *cis*-$ClNO_2$ $>$ *trans*-$ClNO_2$ $>$ *cis*-NH_3NO_2 $>$ *trans*-NH_3NO_2 $>$ *trans*-$(NCS)NO_2$. The *trans*-dinitro complex reacts in much more dilute acid than the *cis* analogue, exemplifying the high *trans* effect of a nitro group. When the directing ligand is chloro or ammine, the members of a *cis* and *trans* pair react at rates which are within a factor of ten. In the ammine case the ratio of rates *cis*/*trans* (= 6) shows that although the two complexes are very similar and are analogous to the ion $[Co(NH_3)_5NO_2]^+$ the NH_3 and en ligands have slightly different inductive and *trans*-effects. When the isothiocyanato ligand is the directing group the difference in reactivities of the two isomers is vast, the *trans* compound reacting much more slowly. This phenomenon has also been noticed in the study of basic hydrolysis and aquation, an isothiocyanato ligand *trans* to the leaving group greatly reduces the rate of hydrolysis[27].

The most illuminating piece of work is that of Harris et al.[28] using the complex ion $[Co(NH_3)_5NO_2]^{2+}$ as substrate. They showed that the mechanism of acid-catalysed hydrolysis of the nitro-group may be described by scheme 6.



Scheme 6. Reproduced from ref. 28 by permission of the authors and *Inorganic Chemistry*.

When the complex ion was hydrolysed in ^{18}O-enriched water, the aquopentamminecobalt(III) product contained only the natural abundance of ^{18}O, i.e. the oxygen atom of the aquo group of the product originates from the nitro group, not from the solvent.

Several studies of the kinetics of the replacement of nitro groups from pentammine complexes have been reported. Harris et al. reported that the observed rate constant k_{obs} is given by eqn. (27)

$$k_{obs} = kh_0 \qquad (27)$$

where $h_0 = -\text{antilog}\, H_0$.

Crossland and Staples[29] studied the acid-catalysed aquation of $[M(NH_3)_5NO_2]^{2+}$ ions (where M = Co, Rh or Ir). No maximum rate constants were observed; even in concentrated sulphuric acid only moderately low degrees of protonation are attained. The cobalt complex is apparently a somewhat stronger base than the rhodium analogue; the iridium complex is an even weaker base. The Arrhenius parameters are given in Table 3. Analysis of the results by the methods of Bunnett and of Zucker and Hammett favours a mechanism in which water is not involved. The results presented by Jolly and by Crossland and Staples do not agree with those reported earlier by Lalor[30]. In this earlier paper the hydrolysis was studied at much higher temperatures and at much lower acid concentrations. The observed rate constant is given by eqn. (28)

$$k_{obs} = k_0 + k_1[H^+] + k_2[H^+]^2 \qquad (28)$$

The activation energies also differ from those of other workers (see Table 3).

The hydrolysis of a series of complex ions, viz. *cis*- or *trans*-$[CoA_4(NO_2)_2]^+$ where A = NH_3, $\frac{1}{2}$(en), $\frac{1}{2}$(tn), $\frac{1}{4}$(cyclam) or $\frac{1}{4}$(trien), at 25°C has been reported[31]. The results may be summarized as follows. (1) No maximum rate constants were observed; (2) the *trans* isomers required less concentrated acid to effect appreciable acid catalysis, i.e. the *trans* isomers are apparently stronger bases than their *cis* analogues; (3) the more highly chelated species, e.g. the cyclam complex, appear to be stronger bases than the less chelated analogues; (4) analysis of the results according to Zucker and Hammett's hypothesis favours a

TABLE 3

Activation parameters for the acid-catalysed hydrolysis of nitro complexes

	E (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal.deg^{-1}.mole^{-1})	Ref.
Reactive species			
trans-$Co(NH_3)_4(NO_2)(NO_2H)^{2+}$	26.2	+7	38, 37
trans-$Co(NH_3)_4(NO_2H)_2{}^{3+}$	18.0	−20	38, 37
trans-$Co(NH_3)_4(NO_2)(NO_2H)^{2+}$, Cl^-	23.6	+4	38
trans-$Co(NH_3)_4(NO_2H)_2{}^{3+}$, Cl^-	23.2	+1	38
trans-$Co(dipy)_2(NO_2)(NO_2H)^{2+}$	34.6		39
trans-$Co(en)_2NO_2(NO_2H)$	23.6	+2.9	33
Complex	E	log A	
cis-$Co(en)_2(NO_2)_2{}^+$	25.6	13.9	23
trans-$Co(en)_2(NO_2)_2{}^+$	24.9	13.7	23
$Co(NH_3)_5NO_2{}^{2+}$	38.8		30
$Co(NH_3)_5NO_2{}^{2+}$	18.0	10.3	29
$Rh(NH_3)_5NO_2{}^{2+}$	16.4	9.1	29

mechanism in which water is not involved. On the basis of these observations the systems which were worthy of more detailed study were chosen.

The complex ions *trans*-$[Co(A_4)(NO_2)_2]^+$ (where A_4 = 1, 4, 8, 11-tetraazacyclotetradecane (cyclam) or 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane (isomer(a)(teta)) are hydrolysed in aqueous solutions of strong acids[32]. The results at −7.5°C show that a maximum rate constant is observed for both ions. However, in contrast to the azido cases listed earlier, the maximum rate constant is not a limiting value but decreases again as the acid concentration is increased further. The value of the maximum rate constant is dependent on the particular acid used. In sulphuric acid solutions the sterically more crowded ion *trans*-$[Co(teta)(NO_2)_2]^+$ reacts about five times as fast as the cyclam analogue. The subsequent decrease in rate may be due to the decrease in activity of water. This is unlikely, however, in view of the Harris-type mechanism. The activity of water would not be expected to influence such a mechanism. An alternative possibility is that the rate constant vs. acid concentration profile behaviour is due to the changes of charge which occur in the rate-determining step. If it is assumed that the transition state is more like the products than the reactants, we may apply the rate equation from the transition state theory, so that in the nitro case

$$k = k_0 \, \frac{f_{SNO_2H^{2+}}}{f_{SOH^+} \, f_{NO^+}} \qquad (29)$$

where S = $[Co(cyclam)(NO_2)]^{2+}$. The changes in the activity coefficients with concentrations are generally as follows. The ratio of activity coefficients of two ions of like charge remains fairly constant as the concentration changes and the activity coefficient of a noncharged species varies very little with concentration. It is interesting therefore, to compare eqn. (29) with the corresponding equation for the reaction of an azido complex (30).

$$k = k_0 \frac{f_{SN_3H^{2+}}}{f_{S^{2+}} f_{HN_3}} \tag{30}$$

Inspection of eqns. (29) and (30) shows that in the latter the ratio of activity coefficients remains fairly constant as the concentration changes and so the maximum rate remains constant as the acid concentration is increased still further. In the nitro case, however, the ratio of the activity coefficients will vary with concentration and the maximum rate constant decreases again as the acid concentration is further increased.

Lambert and Mason studied the loss of nitro ligand from a series of complex ions, viz. *cis-* or *trans-*$[Co(AA)_2(NO_2)_2]^+$ (where AA = en, pn, dipy or 2 NH_3) using different aqueous acids as solvents[33,34]. The kinetic results were analysed by Bunnett's method and Lambert and Mason postulate a bimolecular mechanism. In order to perform a Bunnett-type analysis, however, estimated values of the acid dissociation constants (K_a) of the protonated species had to be used. The values chosen were of the order $K_a \sim 5-10$. These values are rather low considering the concentration of acid required to attain appreciable degrees of protonation. In a similar study[7], however, using the Bunnett-type analysis and a K_a value of ~3,000 the results tended to suggest a unimolecular mechanism, i.e. water not involved in the transition state. The experimental results for the two sets of work agree extremely well. The divergence between the conclusions is due entirely to the different K_a values employed.

A stereochemical study was also performed[35] and the results showed that complex ions of the type *d*(+)-*cis*-$[Co(en)_2XNO_2]^+$, when allowed to aquate in perchloric acid, did so with complete retention of optical configuration. This result may be taken as evidence for a bimolecular mechanism or, much more likely, the intramolecular mechanism postulated by Harris et al. for nitropentamminecobalt(III) ion. The intramolecular-type mechanism postulated in scheme 6 would be expected to lead to complete retention of configuration.

Malik and McAuley[36] have made a detailed study of the reactions of $[Co(NH_3)_2(NO_2)_4]^-$ ion in different aqueous acids ($[H^+]$ = 0.5 to 2.5 *M*). There are small but discernible differences in rate constants for equal concentrations of different acids. These results suggest that ion-pairing is important. In a further set of experiments the rate of hydrolysis in mixtures of acids, i.e. perchloric acid with either nitric or hydrochloric acid ($[H^+]$ = constant = 2.5 *M*) was determined. As perchloric acid is successively replaced by one of the other acids there is a steady decrease in the observed first-order rate constant. Malik and McAuley assumed that in perchloric acid very little ion-pairing exists. The kinetics were interpreted in terms of the following steps (scheme 7).

$$\mathrm{Co(NH_3)_2(NO_2)_4^- + H_2O \xrightarrow{k_0} Co(NH_3)_2(NO_2)_3H_2O + NO_2^-} \tag{31}$$

$$\mathrm{Co(NH_3)_2(NO_2)_3NO_2H + H_2O \xrightarrow{k_1} Co(NH_3)_2(NO_2)_3H_2O + HNO_2} \tag{32}$$

$$\mathrm{Co(NH_3)_2(NO_2)_2(NO_2H)_2^+ + H_2O \xrightarrow{k_2} Co(NH_3)_2(NO_2)_2(NO_2H)(H_2O) + HNO_2} \tag{33}$$

$$\mathrm{Co(NH_3)_2(NO_2)_2(NO_2H)_2^+ \ldots\ldots X^- + H_2O \xrightarrow{k_3} Co(NH_3)_2(NO_2)_2(NO_2H)H_2O^{2+} \ldots. X^- + HNO_2} \tag{34}$$

$(X = Cl^-$ or $NO_3^-)$

Scheme 7.

From scheme 7, the observed first-order rate constant k_{obs} is given by

$$k_{obs} = \frac{(k_0 + k_1K_1[H^+] + k_2K_1K_2[H^+] + k_3K_1K_2K_3[H^+]^2[X^-])}{1 + K_1K_2K_3[H^+]^2[X^-]} \tag{35}$$

where K_1, K_2 and K_3 are the formation constants of monoprotonated, diprotonated and ion-paired forms of complex respectively. Rearrangement of eqn. (35) allows evaluation of $k_3K_1K_2K_3$ which is, in fact, approximately zero. $K_1K_2K_3 = 0.01$ for Cl^- and 0.025 for NO_3^- ion. The contribution from the aquation of ion-pair (34) to the overall kinetics is negligible. Thus although ion-pairs exist in the solution and influence the kinetics the actual hydrolysis of the ion-paired species does not contribute directly to k_{obs}.

The hydrolysis of *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ ion in acidic solutions[37] ($[H^+] = 0.1$ to $1.5\ M$) at constant chloride ion concentration ($[Cl^-] = 2.0\ M$) has been interpreted[38] using a treatment similar to that used above for $[Co(NH_3)_2(NO_2)_4]^-$ ion. The reactive species were the chloride ion-pairs of non-, mono- and di-protonated forms of the complex ion.

The acid-catalysed aquation of *trans*-$[Co(dipy)_2(NO_2)_2]^+$ ion at ionic strength $2.5\ M$ over the acid range $[H^+] = 0.2$ to $2.5\ M$ has been interpreted[39] in terms of the aquation of the complex ion and its monoprotonated form. The rate law is given by

$$\text{Rate} = \frac{(k_1 + k_2[H^+])\ [\text{complex(total)}]}{1 + K[H^+]} \tag{36}$$

where [complex(total)] = [complex] + [protonated complex], K = formation constant of the protonated complex, $k'_2 = Kk_2$, k_1 = rate constant for aquation of complex, and k_2 = rate constant for aquation of protonated complex. The Arrhenius parameters have been evaluated (see Table 3). The *trans-cis* isomerisation of $[Co(dipy)_2NO_2(H_2O)]^{2+}$ ion was studied and the kinetics were interpreted in terms of a mechanism involving $[Co(dipy)_2NO_2(OH)]^+$, $[Co(dipy)_2NO_2(H_2O)]^{2+}$ and $[Co(dipy)_2(NO_2H)(H_2O)]^{3+}$.

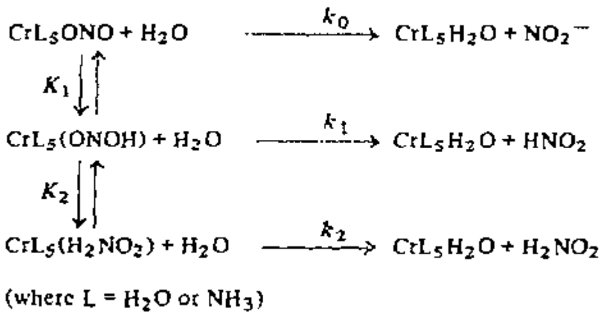
The replacement of nitro groups from platinum(IV) complexes, e.g. 1,6-dibromo-2,3-dinitro-4,5-bispyridineplatinum(IV) is acid-catalysed only at very high acid concentrations[40]. This is attributed to the highly acidic nature of protons of platinum(IV) complexes, i.e. the protonated complex is such a strong acid that very little of the protonated form is present in equilibrium mixtures except at very high acid concentrations. This phenomenon is a feature of platinum(IV) chemistry. Ammine and aquo complexes of platinum(IV) are much stronger acids than corresponding complexes of, say, cobalt(III) or rhodium(III)[41].

(iv) Nitrito complexes

The acid-catalysed aquation of CrL_5ONO^{2+} ions ($L = H_2O$ (ref. 42) or NH_3 (ref. 43)) has been studied in perchloric acid–sodium perchlorate solutions ($I = 1.0$). At higher acidities and temperatures the pentammine complex loses coordinated ammonia. The reaction is first-order in complex ion concentration and the observed first-order rate constant k_{obs} is given by eqn. (28)

$$k_{obs} = k_0 + k_1[H^+] + k_2[H^+]^2 \qquad (28)$$

Matts and Moore favour a mechanism which may be written as scheme 8.



Scheme 8.

They say that the mechanism of acid-catalysed hydrolysis in 0.01–1.0 *M* perchloric acid cannot be the reverse of the mechanism of nitrosation of aquo complexes, at pH 3–4, to yield nitrito compounds. Matts and Moore postulate that at lower pH values nitrosonium ion is the nitrosating agent.

Fee et al.[44] have recently reported the acid-catalysed hydrolyses of a series of nitrito complex ions (see Table 4), viz. *cis-* or *trans-*$\{Cr(en)_2X(ONO)\}^{n+}$ (where X = ONO, F, Cl, Br, H_2O, DMF, DMSO). The kinetic results were similar to those reported by Matts and Moore although the chelated complexes reacted a few times more slowly than the pentammine complexes. Fee et al. postulate a mechanism similar to that of scheme 8. The reactions proceed with ~ 100 per cent retention of geometrical configuration. The position of bond cleavage could not be deduced from ^{18}O experiments because side reactions interfered. Fee et al. argue that enhancement of the rate in acid solution is much greater than that for $Cr(H_2O)_5F^{2+}$, where chromium–ligand fission must occur, that CrO–N bond fission seems more likely, i.e. nitrosonium ion is the leaving group.

TABLE 4

Activation parameters for the acid-catalysed hydrolysis of nitrito complexes[44] ($I = 0.15$)

Complex	$\Delta H^{\ddagger}$ kcal.mole^{-1}	$\Delta S^{\ddagger}$ cal.deg^{-1}.mole^{-1}
trans-$Cr(en)_2(ONO)_2{}^{+}$	24.3	17.6
trans-$Cr(en)_2H_2O(ONO)^{2+}$	19.8	3.2
cis-$Cr(en)_2(ONO)_2{}^{+}$	22	18
cis-$Cr(en)_2H_2O(ONO)^{2+}$	20.1	4.9
trans-$Cr(en)_2Cl(ONO)^{+}$	21.0	4.9
trans-$Cr(en)_2Br(ONO)^{+}$	20.3	3
trans-$Cr(en)_2(ONO)(DMF)^{2+}$	20.1	3.8
trans-$Cr(en)_2(ONO)F^{+}$	20.9	3.4
$Cr(H_2O)_5(ONO)^{2+}$ [a]	19.8	9
$Cr(NH_3)_5(ONO)^{2+}$ [a]	19.7	5

[a] Refers to the doubly protonated species; $I = 1.0$.

TABLE 5

Arrhenius parameters for the acid-catalysed hydrolysis of some nitrito complexes

Complex	E (Kcal.mole^{-1})	log A	Ref.
$Co(NH_3)_5ONO^{2+}$	15.9	9.3	29
$Rh(NH_3)_5ONO^{2+}$	15.7	9.7	29
$Ir(NH_3)_5ONO^{2+}$	16.3	10.3	29
$Cr(H_2O)_5ONO^{2+}$	14.5	11.2 [a]	42, 43

[a] Values refer to second protonation; for first protonation $E = 20.4$; log $A = 15.2$.

The hydrolysis of $M(NH_3)_5ONO^{2+}$ ions (where M = Co, Rh or Ir) in dilute solutions of sulphuric acid (see Table 5) has been studied[29]. The kinetics obey the relationships

$$\log k_{obs} \propto -2H_0 \tag{37}$$

and

$$\log k_{obs} \propto 2 \log[H^+] \tag{38}$$

It is not possible to distinguish between the two relationships because over the range of sulphuric acid concentrations used the rates of change of acidity function and log $[H^+]$ with acid concentration are very similar. However, if the hydrolyses are studied using aqueous perchloric acid–sodium perchlorate solutions ($I = 1.0$) as solvents the relationship

$$\log k \propto \log [H^+] \tag{39}$$

is obeyed. Relationship (39) breaks down at the highest acid concentrations studied; the results show that relationship (38) is becoming important. The equilibria involved are extremely sensitive to added salts. The relationship (37) takes account of changes in activity which occur as the ionic strength changes. These results, together with those of Matts and Moore, strongly suggest that the mechanism for the hydrolysis is not the reverse of the nitrosation of aquo-pentammine salts. The rate laws involved here also suggest that the possible mechanism for the hydrolysis of nitro complexes viz. a prior nitro to nitrito arrangement, does not occur.

Although the Zucker–Hammett hypothesis does not give much information about the possible inclusion of a solvent molecule in the transition state the Bunnett hypothesis favours a mechanism which does not involve water.

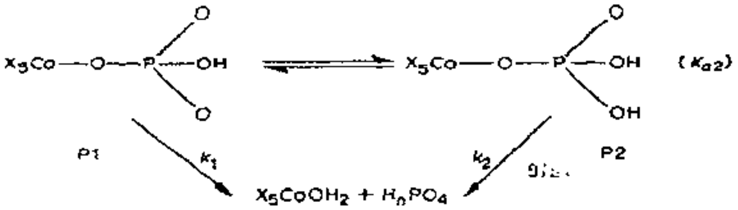
A further point of interest is the similarity in rate constant for the three different central metal ions. This, coupled with the similarity of the Arrhenius parameters, provides evidence for nitrogen–oxygen bond fission as opposed to metal–oxygen bond breaking.

The acid-catalysed aquation of $Co(NH_3)_5ONO^{2+}$ ion is also catalysed by halide or thiocyanate ions[45]. This provides experimental confirmation of the view expressed earlier[32] that anions X may assist removal of nitrosonium ions, in the form NOX, from the complex.

(v) Phosphato complexes

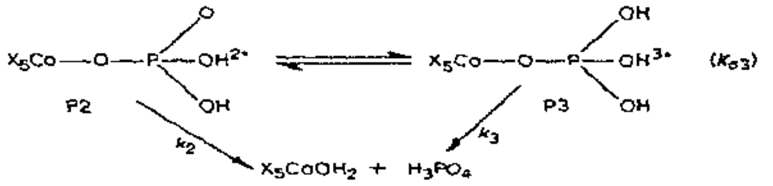
The rate of release of phosphato ligand from a series of its complexes, has been studied over a wide range of acid concentrations (0.001 to 11.4 *M* $HClO_4$). Lincoln and Stranks[46–48] studied the rate of reaction radiochemically by using labelled ^{32}P-phosphate. The rate of reaction is always first-order in complex concentration and the kinetics were studied using three distinct regions of acid concentration. These ranges were chosen after Stranks et al.[46] had carried out equilibrium studies to determine the dissociation constants of the various protonated forms of these complexes (see section F). The reaction scheme may be outlined as in scheme 9.

(*a*) In the range $[HClO_4] = 0.001$ to 0.04 *M* the predominant complexes are P1 and P2 and their concentrations are related by the acidity constant K_{a2}



Scheme 9 (a). Reproduced from refs. 46–48 by permission of the authors and the *Australian Journal of Chemistry*.

(*b*) In the concentration range [$HClO_4$] = 0.05 to 5.0 *M* the predominant species are P2 and P3, both of which react at characteristic rates



Scheme 9 (b). Reproduced from refs. 46–48 by permission of the authors and the *Australian Journal of Chemistry*.

The fact that the different protonated species P1, P2, P3 react at different rates for each of the substrates studied leads to the type of relationship between rate constant and acid concentration which is illustrated in Fig. 2.

For the reaction of species P1, P2, P3 a bimolecular S_N2CA mechanism is postulated because, in the acid region where the substrate is nearly all in the form P3, the rate of hydrolysis is directly proportional to the activity of water, i.e.

$$k_{obs} = k_3 [P3]\, a_{H_2O} \tag{40}$$

Thus k_{obs}/a_{H_2O} is constant over the acid concentration range ca. 2 *M* to ca. 5 *M*.

At acid concentrations above 5 *M* $HClO_4$ the rate constant increases markedly although the activity of water decreases markedly (from 0.61 in 5 *M* $HClO_4$ to 0.05 in 10 *M* $HClO_4$).

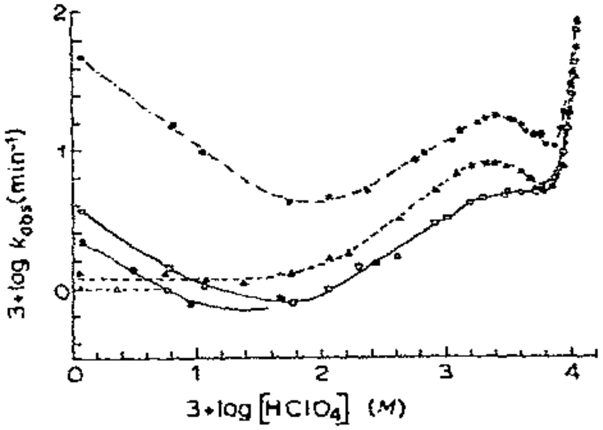


Fig. 2. Rates of hydrolysis of phosphato complexes in aqueous $HClO_4$ at 60°C. (●) $Co(NH_3)_4OH_2PO_4$; (▲) $Co(NH_3)_5PO_4$; (○) $Co(en)_2OH_2PO_4$; (△) 1 *M* $NaClO_4$ medium; (■) 1 *M* $NaClO_4$ medium. Reproduced from refs. 46–48 by permission of the authors and the *Australian Journal of Chemistry*.

The increase in rate was attributed to a fourth tetra-protonated species P4. Even at the highest acid concentrations (11.7 *M*) there was no indication that the fourth protonation was complete. In this acid concentration range log k_{obs} varies linearly with the H_0 acidity function and a unimolecular S_N1CA mechanism was postulated for this step.

It is noteworthy that chelated phosphato complexes react as rapidly as their monodentate counterparts because of the rapid conversion of chelated to monodentate phosphato linkages. The values of the hydrolysis constants for the series of complexes is given in Table 6.

In a further series of experiments using $H_2{}^{18}O$ as solvent (Table 7) it was shown that the hydrolysis of $Co(NH_3)_5PO_4$ and $Co(en)_2(H_2O)PO_4$ in acidic solutions occurred by 100% cobalt–oxygen bond fission; the phosphate released contained only the natural abundance of ^{18}O oxygen.

TABLE 6

Rate constants (sec^{-1}) for the hydrolysis of the various protonated forms of some phosphato complexes in aqueous perchloric acid at 60.0°C

Complex	10^5k	10^5k_2	10^5k_3	10^5k_4 [a]	Supporting electrolyte
$Co(NH_3)_4$	123	4.2	33	5.5 [a]	None
$Co(en)_2$	9.2	0.67	9.2	15.4 [a]	None
$Co(en)_2$	5.5	0.47			1 *M*-$NaClO_4$
$Co(NH_3)_5$	2.0	2.0	15		None
$Co(NH_3)_5$	1.6	2.0			1 *M*-$NaClO_4$

[a] Rate constants using 11.4 *M* $HClO_4$ in which the tetraprotonated species are incompletely formed. The subscript of the rate constant denotes the degree of protonation of the phosphato ligand.

TABLE 7

Activation parameters for the hydrolysis of protonated phosphato complexes in aqueous perchloric acids

Complex	*E* (kcal·mole^{-1})	$\Delta H^{\ddagger}(60°)$ (kcal·mole^{-1})	$\Delta S^{\ddagger}(60°)$ (cal·deg^{-1}·mole^{-1})
$Co(NH_3)_5PO_4H_3{}^{3+}$	26.3	25.6	−7.4
$Co(NH_3)_5PO_4H_4{}^{4+}$	23.5		
$Co(NH_3)_4OH_2.PO_4H_3{}^{3+}$	25.6	24.9	−7.8
$Co(NH_3)_4OH_2.PO_4H_4{}^{4+}$	25.0		
$Co(en)_2OH_2.PO_4H_3{}^{3+}$	25.6 [a] 26.1 [b]	24.9	−8.3
cis-$Co(en)_2NH_3PO_4H_3{}^{3+}$ [c]		27.1	−2.6
trans-$Co(en)_2NH_3PO_4H_3{}^{3+}$ [c]		27.0	−2.6

[a] In 4.0 *M* $HClO_4$.
[b] In 10.4 *M* $HClO_4$.
[c] At 70°C.

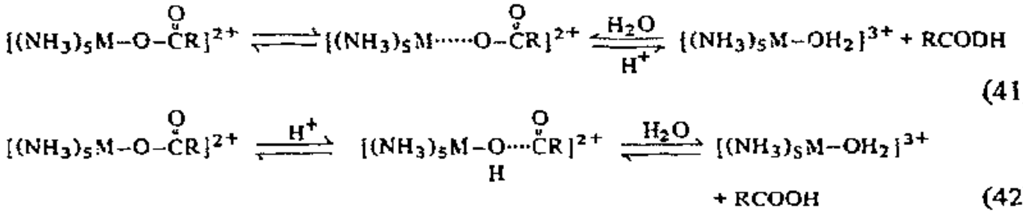
Lincoln and Purnell[49] have reported the acid-catalysed aquations of *cis*- and *trans*-$Co(en)_2NH_3PO_4$. The triprotonated species aquate with cobalt—oxygen bond fission and with complete retention of configuration. It was pointed out that this retention of configuration is characteristic of systems of the $Co(en)_2NH_3X$ type which are considered to aquate via a dissociative mechanism. It was therefore suggested that this was the likely mechanism in this case.

(vi) Acetato complexes

The hydrolysis of $[M(NH_3)_5(OOC.R)]^{2+}$ ions (where M = Co, Rh or Ir and R = CH_3, $C(CH_3)_3$ or CF_3) is acid-catalysed[50] ($[H^+] = 0.008$; 0.10 *M* $NaClO_4$). At lower acid concentrations the aquation reaction is the sole pathway. The observed rate law is

$$k_{obs} = k_{H_2O} + k_{H^+}[H^+] \tag{23}$$

and this would be in accord with either of the two possible mechanisms. It is noteworthy that the two possible pathways postulated involve the breaking of different bonds (eqns. (41) and (42)).



$$[(NH_3)_5M-O-\overset{O}{\overset{\|}{C}}R]^{2+} \rightleftharpoons [(NH_3)_5M\cdots\cdots O-\overset{O}{\overset{\|}{C}}R]^{2+} \underset{H^+}{\overset{H_2O}{\rightleftharpoons}} [(NH_3)_5M-OH_2]^{3+} + RCOOH \tag{41}$$

$$[(NH_3)_5M-O-\overset{O}{\overset{\|}{C}}R]^{2+} \overset{H^+}{\rightleftharpoons} [(NH_3)_5M-\underset{H}{O}\cdots\overset{O}{\overset{\|}{C}}R]^{2+} \overset{H_2O}{\rightleftharpoons} [(NH_3)_5M-OH_2]^{3+} + RCOOH \tag{42}$$

Scheme 10.

An attempt was made to distinguish between these two possibilities, i.e. the experiments were repeated using oxygen-18 water as the solvent. Although isotopic enrichment was found in the product the experiments do not provide proof of acyl—oxygen bond fission because the aquo product exchanges with the solvent under the relevant experimental conditions. There is, however, one further piece of evidence which favours acyl—oxygen bond rupture, i.e. for a given alkyl group the rate constants k_{H^+} are very similar for all three metals studied. In reactions known to involve cleavage of a metal—ligand bond, e.g. hydrolysis of $M(NH_3)_5Br^{2+}$ ions[51], the rate constants are in the ratio Co : Rh : Ir = 4000 : 1000 : 1.

An elegant study of the reactions of acetatopentaaquochromium(III) ion has been reported[52]. At ionic strength $I = 1.00$ the rate constant increases linearly with the acid concentration and over the acid concentration range $[H^+] = 0.040$ to 0.970 *M* the rate law (eqn. (43)) is obeyed. However, at ionic strength $I = 4.0$ this relationship (43) breaks down at higher acid concentrations, the increase in rate constant does not keep pace with the increase in the acid concentration as predicted by the rate eqn. (43).

$$k_{\text{obs}} = \frac{k_1 + (k\ \text{H}^+/K_a)}{1 + (\text{H}^+/K_a)} \tag{43}$$

In aqueous perchloric acid, without added salts, a plot of k_{obs} vs. perchloric acid concentration shows a maximum at ca. 5 *M* perchloric acid. The maximum rate constant is not, however, limiting; it subsequently decreases as $[\text{HClO}_4]$ is further increased. Over the range $[\text{HClO}_4] = 6–8$ *M*, there is a direct relationship between the rate constant and the activity of water. At higher acid concentrations, however, the correlation breaks down. The Arrhenius parameters (Table 8) were interpreted as support for acyl—oxygen bond fission. The dissociation constant K_a of the conjugate acid was evaluated at different ionic strengths (Table 9).

TABLE 8

Activation parameters for the acid-catalysed hydrolysis of acetato complexes in aqueous perchloric acid

Complex substrate	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal.deg^{-1}.mole^{-1})	I	Ref.
$[\text{Co(NH}_3)_5\text{CH}_3\text{COO}]^{2+}$	25	+2	0.10	50
$[\text{Co(NH}_3)_5\text{C(CH}_3)_3\text{COO}]^{2+}$	26	+6	0.10	50
$[\text{Rh(NH}_3)_5\text{CH}_3\text{COO}]^{2+}$	23	−4	0.10	50
$[\text{Rh(NH}_3)_5\text{C(CH}_3)_3\text{COO}]^{2+}$	23	−6	0.10	50
$[\text{Ir(NH}_3)_5\text{CH}_3\text{COO}]^{2+}$	25 [a]	−8	0.10	50
$[\text{Ir(NH}_3)_5\text{CF}_3\text{COO}]^{2+}$	14	−36	0.10	50
$[\text{Cr(H}_2\text{O)}_5\text{CH}_3\text{COO}]^{2+}$	18.6		4.0	52
cis-$[\text{Co(en)}_2(\text{CH}_3\text{COO})_2]^+$	15.4	−13	2.0	53
trans-$[\text{Co(en)}_2(\text{CH}_3\text{COO})_2]^+$	23.0	+1	2.0	53

[a] Determined from data at only two temperatures.

More recently, however, the acid-catalysed hydrolysis of some acetato-bisethylenediaminecobalt(III) complexes has been studied[53] and the results do not provide evidence for acyl—oxygen bond fission. Dasgupta and Tobe[53] found that *trans*-$[\text{Co(en)}_2(\text{OAc})_2]$

TABLE 9

Dissociation constants of protonated acetato complexes, determined kinetically from eqn. (43)

Complex	K_a	Comments
$[\text{Cr(H}_2\text{O)}_5\text{AcOH}]^{3+}$	3.2	$I = 4.0$
	1.3	$I = 5.2$
	0.4	$I = 6.0$
trans-$[\text{Co(en)}_2(\text{AcO})(\text{AcOH})]^{2+}$	1.05	$I = 2.0$; 39.0°
	1.22	$I = 2.0$; 50.0°
cis-$[\text{Co(en)}_2(\text{AcO})(\text{AcOH}]^{2+}$	6.5	$I = 2.0$; 39.0°
	7.4	$I = 2.0$; 50.0°

yields 25% *trans*-acetato aquo complex and 75% *cis* product. The *cis*-diacetato complex is more labile than the *trans* analogue and is hydrolysed with complete retention of configuration. That the *trans* substrate does not hydrolyse with retention of configuration may be used as evidence against acyl—oxygen bond fission. A dissociative mechanism involving cobalt—oxygen bond fission was preferred. However, isotopic labelling experiments would probably resolve the controversy concerning the position of bond fission.

A further point of interest is that Tobe et al. find that for *cis*-$[Co(en)_2(OAc)_2]^+$ ion the rate constant reaches a maximum value in ca. 0.30 *M* $HClO_4$ ($I = 2.0$) and the k_{obs} remains unchanged over the range $[H^+] = 0.30-1.00$ *M*. Deutsch and Taube[52], however, found that the rate constant for the hydrolysis of $[Cr(H_2O)_5(OAc)H]^{3+}$ reaches a maximum value ($HClO_4 \sim 5$ *M*) and then decreases again. However, care should be taken when drawing mechanistic conclusions from such a comparison. In particular, solutions of varying acidity but constant ionic strength have almost constant water activity values. Thus in the study of *cis*-$[Co(en)_2(OAc)_2]^+$ the water activity was constant throughout, whereas for $[Cr(H_2O)_5(OAc)]^{2+}$ it was not.

(vii) Cyano complexes

Adamson et al.[54] found that the ion $Cr(CN)_6{}^{3-}$ was not very stable in solutions of low pH and that the decomposition reaction interfered with cyanide exchange studies. Later the whole series of complex ions, viz. $Cr(CN)_5H_2O^{2-}$, *cis*-$Cr(CN)_4(H_2O)_2{}^-$, 1,2,3-$Cr(CN)_3(H_2O)_3$, *cis*-$Cr(CN)_2(H_2O)_4{}^+$ and $Cr(CN)(H_2O)_5{}^{2+}$ was prepared[55] and the members separated by ion exchange. Wakefield and Schaap[56–58] have studied the acid-catalysed hydrolyses of some of these compounds. In each case there is a small background aquation. The kinetics fit eqn. (44) where K_1 is the *formation* constant of the appropriate protonated form.

$$k_{obs} = \frac{(k_0 + k_1 K_1 [H^+])}{1 + K_1 [H^+]} \tag{44}$$

The postulated mechanism is

$$cis\text{-}Cr(H_2O)_4(CN)_2{}^+ + H^+ \xrightleftharpoons{K_1} cis\text{-}Cr(H_2O)_4(CN)(CNH)^{2+} \tag{45}$$

$$cis\text{-}Cr(H_2O)_4(CN)(CNH)^{2+} + H_2O \xrightarrow{k_1} Cr(H_2O)_5CN^{2+} + HCN \tag{46}$$

In the case of the dicyano complex[57] there was possibly a small contribution from a diprotonated species. However, in the case of the tricyano complex[58] there is a more significant contribution from the diprotonated form, and the kinetics follow a more complicated form of eqn. (44) to take account of the second protonation. Some activation parameters for these reactions are collected in Table 10. The ΔH values are the same for all three aquocyano species.

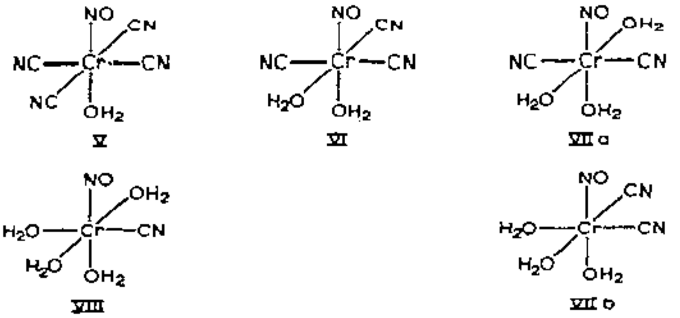
TABLE 10

Activation parameters for the monoprotonated forms of $Cr(CN)_n(H_2O)_{6-n}^{(3-n)+}$

Complex	$\Delta H^{\ddagger}$ (kcal·mole^{-1})	$\Delta S^{\ddagger}$ (cal·deg^{-1}·mole^{-1})	K_a [a]
$Cr(H_2O)_5CN^{2+}$	16	−16	5.4 (I = 2.0)
cis-$Cr(H_2O)_4(CN)_2{}^+$	16	−18	4.8 (I = 2.0)
1,2,3-$Cr(H_2O)_3(CN)_3$	16	−19	
$Cr(CN)_5NO^{3-}$	19		0.0011 (I = 1.0) T = 17.5°C

[a] K_a is the acid dissociation constant of the monoprotonated form, calculated from the literature values of the formation constants at 25.0°C.

Burgess et al.[59] studied the hydrolyses of $Cr(CN)_5NO^{3-}$ ion and detected some of the intermediates using electron spin resonance. In perchloric acid (0.05–1.60 *M*) the rates of the earlier steps are too fast to follow kinetically and ESR signals were not observed for species V and VI (of scheme 11) in any runs. The kinetics of the changes VII → VIII → $Cr(H_2O)_5NO$ were studied and from the ESR and kinetic results it was possible to assign configurations to some of the species involved. The configurations are shown in scheme 11. The pK_a values of species VII and VIII are 1.2 and 0.7 respectively.



Scheme 11. Reproduced from ref. 59 by permission of the authors and the Chemical Society (London).

The same reaction was studied using only mildly acidic solutions[60], the product being $Cr(CN)_2(H_2O)_3NO$ which does not react further under these conditions. Thus the earlier steps could be studied.

The mechanism of the dissociation of $Ni(CN)_4{}^{2-}$ ion in acid solutions has been reported. Kolski and Margerum[61] postulate the mechanism (scheme 12) which is consistent with the observed kinetics.

$$Ni(CN)_4{}^{2-} + H^+ \xrightleftharpoons{K_H} HNi(CN)_4{}^-$$

$$HNi(CN)_4{}^- + H^+ \xrightleftharpoons{K_{2H}} H_2Ni(CN)_4 \xrightarrow{k_{2H}} \text{products}$$

$$H_2Ni(CN)_4 + H^+ \xrightleftharpoons{K_{3H}} H_3Ni(CN)_4{}^+ \xrightarrow{k_{3H}} \text{products}$$

$$H_3Ni(CN)_4 + H^+ \xrightleftharpoons{K_{4D}} H_4Ni(CN)_4{}^{2+} \xrightarrow{k_{4D}} \text{products}$$

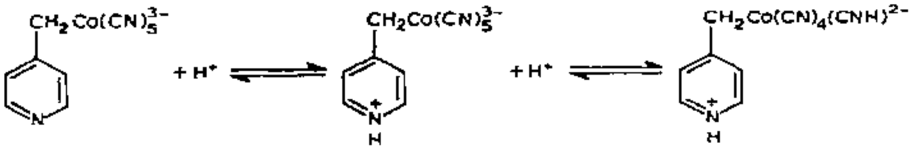
Scheme 12.

This mechanism gives the following expression for the rate of dissociation k_d.

$$k_d = \frac{K_H K_{2H} k_{2H} [H^+]^2 + K_H K_{2H} K_{3H} k_{3H} [H^+]^3 + K_H K_{2H} K_{3H} K_{4H} k_{4H} [H^+]^4}{1 + K_H [H^+] + K_H K_{2H} [H^+]^2 + K_H K_{2H} K_{3H} [H^+]^3} \qquad (47)$$

Equation (47) fits the observed kinetics over the acid range studied. As no final maximum rate constant was observed K_{4H} could not be determined. K_H and K_{2H} were checked by spectrophotometry (Table 11) and the values so obtained are $\log K_H = 5.4$ and $\log K_{2H} = 4.5$.

Johnson et al.[62] showed that the hydrolysis of 4-pyridylmethylpentacyanocobaltate(III) ion, IX, is acid-catalysed. In solutions of pH 9.2 and below, the pyridine ring is protonated to form 4-pyridiomethylpentacyanocobaltate(III) ion, X, and in perchloric acid (ca. 4 *M*) a second proton is added, presumably to one of the cyano ligands. The protonation scheme may be written



IX X XI

Scheme 13.

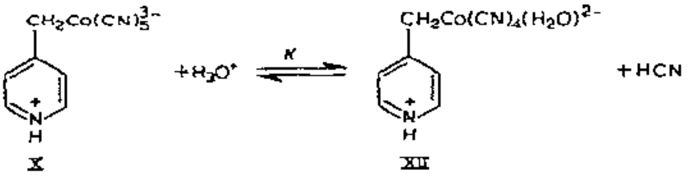
TABLE 11

Parameters for the successive protonation (scheme 12) of $Ni(CN)_4{}^{2-}$ ion at 25.0°

$\log K_H$	$\log K_H K_{2H}$	$\log K_{3H}$	$10^4 k_{3H}$ (sec^{-1})	$10^4 k_{2H}$	$K_{4H} k_{4H}$ (mole^{-1}.sec^{-1})
5.4	9.9	2.6	5.2	0.92	3.3×10^{-3}

[a] Note that K_H is a formation constant.

The pK_a value of the protonated form XI, defined as the acidity at which the complex is exactly fifty percent protonated, is -2.0 ± 1.0 (based on the H_- scale for perchloric acid). The protonated species X has a pK_a value = 9.2. That the first protonation site is the nitrogen atom of the pyridine ring has been substantiated by NMR studies. In addition to the above rapidly established acid–base equilibria there is a slow solvolysis that becomes perceptible at pH < 6 and results in the loss of one cyano ligand and the reversible formation of pyridiomethylaquotetracyanocobaltate(III) anion XII. However, study of the equilibrium is complicated by further decomposition of XII. The equilibrium between X and XII may be written as



(48)

The value of the equilibrium constant was deduced from the kinetics and log $K = -1.6 \pm 0.5$.

The decomposition reactions depend on the pH of the solution and two types of behaviour were described.

(1) pH < 0. The decomposition of the species IX in perchloric acid (1.0 to 9.3 *M*). The slow changes in the absorption spectra are consistent with breaking of the Co–CH_2 bond and the only product isolated from 2.6 *M* perchloric acid was a 4-cyanomethylpyridinium salt. The following possible products were absent, viz. 4-methylpyridinium ion; 4,4′-dipyridylethane and pyridine-4-aldehyde. The most important features are (*a*) the rate constant reaches a limiting maximum value in perchloric acid more concentrated than 7.5 *M*; (*b*) the maximum rate constant is twice that for a solution of acidity $H_- = -1.6$, i.e. the so-called "pK_a value" of species X (eqn. 48); and (*c*) below $H_- = 2$, log *k* is a linear function of $-H_-$ with slope ca. 0.8. It should be pointed out that H_- has been used throughout this work when H_{2-} or H_{3-} would have been strictly more relevant. However, H_- is much better documented in the literature. The results were interpreted in terms of a unimolecular breakdown of the protonated pyridiomethylpentacyanocobaltate(III) ion XI. Finer points of the mechanism could not be decided. For instance, does the insertion of cyanide involve the protonated or one of the unprotonated cyano-ligands and is the protonated cyano group *cis* or *trans* to the pyridiomethyl group? The products suggest that a dissociative process involving complete separation of the fragments could be ruled out because (*a*) no pyridine-4-aldehyde is formed when oxygen is bubbled through the solution and oxygen is known to be an effective trap for pyridiomethyl radicals; (*b*) any carbonium ion or carbanion formed from heterolytic bond fission would be consumed immediately by the solvent to give 4-pyridiomethanol or 4-methylpyridinium cation respectively; neither of these is formed. The formation of 4-cyanomethylpyridinium cation appears to be an "insertion" reaction.

(2) At lower acidities (pH 1–5) the kinetics are complicated by the slowly established equilibrium between the penta- and tetra-cyano species X and XII, and by the further decomposition of the latter ion at a rate comparable with the initial rate of approach to equilibrium. The kinetics can be simplified by addition of small quantities of HCN sufficient to suppress the formation of the aquo-tetracyano complex so that only the acid-catalysed decomposition of the pentacyano-species is observed. As the pH is raised the mechanism changes. At pH 3 the product is pyridinium-4-aldehyde ion. The aldehyde would be the expected product if there is homolytic fission of Co–CH$_2$ bond and the 4-picolinium ion would result from heterolytic fission. The results suggest that in solutions of pH 3 both homolytic and heterolytic fission of the aquotetracyano species may be important.

(viii) Amine complexes

The aquations of Ru(NH$_3$)$_6{}^{2+}$ and Ru(NH$_3$)$_5$py^{2+} are acid-catalysed[63]. The rate is first-order in both complex and acid concentrations. The ion Ru(NH$_3$)$_5$py^{2+} reacts at a somewhat slower rate than the hexammine complex. Electron-withdrawing groups in the pyridine ring stabilise the complexes giving rise to slower rates of aquation. The observed rate constants (2.00 *M* HCl) vary with ring substituent as follows.

p-CH$_3$ $>$ m-CH$_3$ $>$ H $>$ m-Cl $\sim$ m-COOCH$_3$

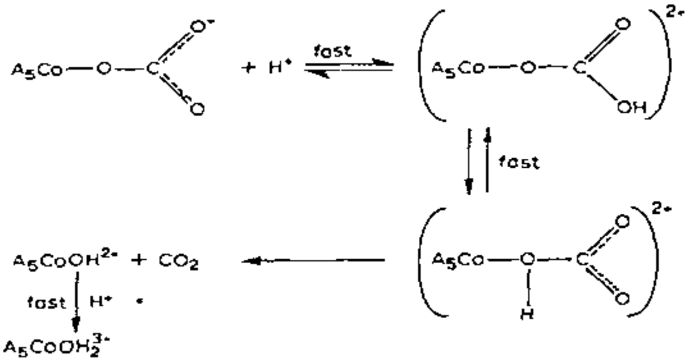
However, in the case of the unsubstituted pyridine complex it was shown that there is a parallel loss of pyridine and ammonia.

In contrast the replacement of ammonia from Ni(NH$_3$)$_6{}^{2+}$ (ref. 64) and Cr(NH$_3$)$_6{}^{3+}$ (ref. 65) is not acid-catalysed. The coordinated ammonia ligand has no free electron pairs to act as possible protonation sites. Ford et al.[63] postulate that the protons attack the metal of Ru(NH$_3$)$_6{}^{2+}$. The faces of the octahedron are electron-rich. Taube has pointed out that such a phenomenon is much more likely for a second or third row transition element than for one in the first row because the π d-electrons extend relatively further into and beyond the first coordination sphere. The relative basicities of the complexes in the series have been discussed.

The complex ions Re(amine)$_4$O$_2^+$ (where amine = pyridine or $\frac{1}{2}$(ethylenediamine)) react with dilute and concentrated hydrochloric acid to yield Re(amine)$_2$Cl$_2$O(OH) and Re(amine)$_2$Cl$_2$(OH)$_2$Cl respectively[66]. The ion Re(en)$_2$Cl$_2$(OH)$_2^+$ reacts further with concentrated hydrochloric acid to produce ReCl$_4$(OH)$_2^-$ ion. The rate constants for the replacement of the two ethylenediamine ligands were measured. The kinetics follow the form described by Harcourt and Esson[67] for successive first-order reactions. Starting from Re(en)$_2$(OH)$_2$ ion the two rate constants derived from the Harcourt and Esson treatment of the results are very similar. The rate of removal of the second ethylenediamine ligand was checked by experiments using a salt of the intermediate Re(en)Cl$_2$(OH)$_2^+$ as starting material. The second ethylenediamine molecule is replaced at a rate similar to that of the first not "instantaneously". The activation energies of the two steps ($E \sim 25$ kcal.mole^{-1}) are very similar and so are the log A values (i.e. 13.8 for step 1 and 13.7 for step 2). The results also show that the reactivity of ethylenediamine is not affected by changing the *trans*-ethylenediamine ligand for two chloro groups. It also adds support to the idea that the electronic levels of the rhenium ion are determined primarily by the two oxygen ligands.

(ix) Carbonato and bicarbonato complexes

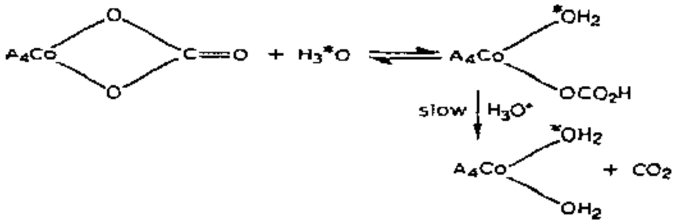
The acid-catalysed hydrolysis of both chelated[68] and monodentate[69] carbonato compounds has been investigated. A study of the ion $[Co(NH_3)_5CO_3]^+$ using isotopically labelled water has shown that carbon—oxygen bond-breaking occurs but not cobalt—oxygen[69]. This means that a bicarbonato complex is the reactive species. The proposed reaction scheme is



Scheme 14.

Similar studies[68] have been performed using the chelated complex, $Co(NH_3)_4CO_3^+$. When this complex is hydrolysed using ^{18}O-labelled water the product is diaquo complex which has half its oxygen derived from the solvent. Thus scheme 15 appears reasonable. In this mechanism there are two bond-breaking steps: (1) cobalt—oxygen and (2) carbon—oxygen. The second bond-breaking is similar to the one which occurs in the monodentate case.

Harris and coworkers[70–75] have made a detailed study of the hydrolysis of a whole series of carbonato complexes of the type $CoN_4CO_3^+$ with particular reference to the effects of different directing groups N_4. In a study[71,72] in which $N_4 = (NH_3)_4$, $(en)_2$, $(pn)_2$ and $(tn)_2$ the rate-determining step in the acidity range $2 < pH < 5$ is the opening of the chelated carbonato ring catalysed by water and hydroxonium ion. The kinetic results for all the systems which have been studied may be explained on the basis of the mechanism



Scheme 15.

set out in scheme 16, if it is assumed that $k_2 \gg k_1[\mathrm{H}^+]$.

$$\mathrm{CoN_4CO_3}^+ + \mathrm{H_2O} \longrightarrow cis\text{-}\mathrm{CoN_4(OH)(CO_3H)}^+ \; (k_0) \tag{49}$$

$$\mathrm{CoN_4CO_3}^+ + \mathrm{H_3O}^+ \longrightarrow cis\text{-}\mathrm{CoN_4(OH_2)(CO_3H)}^{2+} \; (k_1) \tag{50}$$

$$cis\text{-}\mathrm{CoN_4(OH_2)(CO_3H)}^{2+} + \mathrm{H_2O} \rightleftharpoons cis\text{-}\mathrm{CoN_4(OH)(CO_3H)} + \mathrm{H_3O}^+ \; (K_1) \tag{51}$$

$$cis\text{-}\mathrm{CoN_4(OH_2)_2}^{3+} + \mathrm{H_2O} \rightleftharpoons cis\text{-}\mathrm{CoN_4(OH)(OH_2)} + \mathrm{H_3O}^+ \; (K_2) \tag{52}$$

$$cis\text{-}\mathrm{CoN_4(OH_2)(CO_3H)}^{2+} \longrightarrow cis\text{-}\mathrm{CoN_4(OH)(OH_2)} + \mathrm{CO_2} \; (k_2) \tag{53}$$

Scheme 16.

The proposed scheme[73] is a slight modification of previous postulates from Harris and coworkers. In earlier proposals the product of the first step in the scheme was thought to be the aquocarbonato complex. However, recent measurements[75] provide strong evidence for the hydroxo-bicarbonato formulation.

For the tren complex[73] k_1 is large enough and k_2 small enough so that at high acidity the rate of decarboxylation no longer exceeds that of the acid-catalysed opening of the carbonato-chelate ring. Thus the dechelated aquocarbonato intermediate was detected in stopped flow experiments[73].

The observed rate constant for the $\mathrm{Co(tren)CO_3}^+$ complex approaches a limiting value (1.5 sec^{-1}) in 2 M perchloric acid and this corresponds to a decrease in the value of the second-order rate constant k_1 in this range of acidity. This is not due to a concurrent increase in ionic strength since k_1 is known to increase with increasing ionic strength. These observations have been attributed to the fact that in 2 M acid $k_1[\mathrm{H}^+]$ becomes of the same order of magnitude as k_2 and a successive first-order reaction system becomes operative, i.e.

$$\mathrm{Co(tren)CO_3}^+ + \mathrm{H_3O}^+ \xrightarrow{k_1[\mathrm{H}^+]} cis\text{-}\mathrm{Co(tren)(OH_2)(CO_3H)}^{2+} \xrightarrow{k_2} cis\text{-}\mathrm{Co(tren)(OH)(OH_2)} + \mathrm{CO_2} \tag{54}$$

TABLE 12

Rate parameters for the aquation reactions of various $CoN_4CO_3^+$ complex ions at 25°C and ionic strength = 0.5 *M*. Reproduced from ref. 73 by permission of the authors and the American Chemical Society

N_4	$10^4 k_0$ sec^{-1}	$\Delta H_0^‡$ kcal·mole^{-1}	$\Delta S_0^‡$ e.u.	k_1 mole^{-1}·sec^{-1}	$\Delta H_1^‡$ kcal·mole^{-1}	$\Delta S_1^‡$ e.u.
$(NH_3)_4$	1.3 ± 0.2	12 ± 5	−37 ± 19	1.5 ± 0.1	15.3 ± 1.0	− 6.3 ± 3.8
$(en)_2$	1.2 ± 0.2	18 ± 3	−15 ± 9	$0.6 \pm 0.0_5$	13.8 ± 1.0	− 7.4 ± 3.0
$(pn)_2$	1.0 ± 0.2	18 ± 3	−15 ± 9	$0.5 \pm 0.0_5$	14 ± 3	−13 ± 9
$(tn)_2$	0.8 ± 0.2	16 ± 3	−21 ± 9	$0.8 \pm 0.0_5$	12 ± 3	−19 ± 9
tren	1.7 ± 0.2	15 ± 2	−25 ± 5	$2.0 \pm 0.0_5$	11.1 ± 1.0	−20.0 ± 4.0
cis-Diammine	$0.3 \pm 0.1_5$	17 ± 5	−24 ± 12	$0.9 \pm 0.0_5$	16.0 ± 1.0	− 4.0 ± 3.0
trans-Diammine	1.1 ± 0.6	19 ± 5	−14 ± 12	8.9 ± 0.3	10.0 ± 1.0	−20.0 ± 3.0
α-trien	1.5 ± 1.2	20 ± 3	− 7 ± 7	5.2 ± 0.1	15.0 ± 1.0	− 5.0 ± 3.0
β-trien	$0.1 \pm 0.0_7$	17 ± 3	−23 ± 9	$0.2 \pm 0.0_2$	17.0 ± 1.0	− 5.0 ± 3.0
trans-[1,4]diene				(0.008)	(24)	
tetb				(10^{-4})		
$(dipy)_2$				(10^{-4})	(22.3)	(−1.5)
$(phen)_2$				(10^{-4})	(20.4)	(−8.6)

This interpretation is supported by the following evidence: k_1 is known from accurate determinations at lower acidities to be 2 M^{-1}.sec^{-1}, which means that in 2 M acid k_1 [H$^+$] = 4 M^{-1}.sec^{-1}, compared with the decarboxylation rate constant $k_2 \sim 1$ sec^{-1}. A comparison of the rate constants for the different complexes is interesting (see Table 12). For $N_4 = (NH_3)_4, (en)_2, (pn)_2, (tn)_2$, *cis*-$(NH_3)_2$en, *trans*-$(NH_3)_2$en, α-trien and tren, the k_0 values are all very similar (around 1.1×10^{-4} sec^{-1}). It should be pointed out that there is some uncertainty in the k_0 values due to the method of derivation, i.e. a rather small intercept after a large extrapolation. The only member which appears to be exceptional is the β-trien complex in which none of the amine bridges is coplanar with the carbonato chelate ring, in contrast to tren and α-trien. The way in which the (β-trien) amine ligand is disposed (wrapped around) about the complex results in a reduction of strain in the carbonato chelate ring thus inhibiting cleavage of to cobalt–oxygen bond in a manner not possible for the other complexes.

The values of k_1 are also very interesting (Table 12). For $N_4 = (NH_3)_4, (en)_2, (pn)_2, (tn)_2$ and *cis*-$(NH_3)_2$en the k_1 values are all within a factor of 3 with mean $\Delta H^{\ddagger}$ = 16 kcal.mole^{-1} and $\Delta S^{\ddagger} = -6$ e.u. The k_1 value for N_4 = tren is similar to that for the above five complexes. The lower $\Delta H^{\ddagger}$ value for tren complexes is attributed to carbonato ring strain. There are interesting differences, however, for *cis*- and *trans*-isomers of $N_4 = (NH_3)_2$en (where k_1 *trans*/*cis* = 10) and for the isomeric pair N_4 = α-trien and β-trien ($k_1 \alpha / k_1 \beta = 26$). These differences are attributable to the contrast between coplanar and diagonal orientations of amine and carbonato chelate rings. The hydroxonium ion attack (reaction 51, scheme 16) is facilitated by greater carbonato ring strain in the coplanar species, i.e. *trans*-$(NH_3)_2$en and α-trien, and is also accompanied by a lower $\Delta H^{\ddagger}$ value, as is the case for the tren complex. The β-trien complex has an unusually low k_1 value even on the basis of the foregoing explanation, suggesting other factors are important. In this case it has been suggested that the donor oxygen atoms of the carbonato ligand are protected from attack by H_3O^+ by the β-trien in the way it is "wrapped around" the complex. If such a postulate is true then tetradentate ligands which could offer far greater steric hindrance should retard the ring opening process even more. This has been confirmed by later work[76]. For the complexes in which N_4= 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tetb) or its 4, 11-diene analogue (*trans*-[1,4]-diene) the k_1 values are further reduced (cf. trien) (see Table 12). Even with $N_4 = (dipy)_2$ or $(phen)_2$ the ring opening process is greatly retarded.

The aquations of $Co(phen)_2CO_3$ and $Co(dipy)_2CO_3$ in ^{18}O-enriched water[77] suggest that the rate-controlling process is the ring-opening step. The rates of acid-catalysed aquation are unusually low; Francis and Jordan[77] attribute this to the relatively low net electron donation from amine to cobalt making cobalt–oxygen bond fission more difficult than in the cases of aliphatic amines. This view is supported by correlations between rate constants and (1) amine basicity and (2) the relative pK_a values of the series *cis*-$N_4Co(H_2O)_2$. This is not considered to agree entirely with Endicott's postulate that steric and ring strain factors cause the low rates of aquation observed, e.g. $Co(teta)CO_3^+$.

It is interesting to note that the maximum rate constant for carbonato complexes is limiting[73] as in the case of azido complexes and in contrast to nitro complexes. This observation is in accord with the postulate that if the leaving entity is a neutral molecule, e.g. HN_3 from azido complexes or CO_2 from carbonato complexes, the maximum rate is limiting, whereas if the leaving group is an ion e.g. for instance NO^+ from nitro complexes, the maximum rate is non-limiting, i.e. further increases in the acid concentration cause a decrease in the observed rate constant.

(x) Oxalato and hydrogen oxalato complexes

Taube[78] prepared and characterised the ion $[(NH_3)_5Co(C_2O_4)H]^{2+}$. The acid dissociation constant was evaluated spectrophotometrically $K_a = 8.8 \times 10^{-3}$. The hydrolysis of the ion is acid-catalysed. At many of the acid concentrations used, the complex was present in both forms, i.e. $Co(NH_3)_5(C_2O_4)^+$ and $Co(NH_3)_5(C_2O_4)H^{2+}$ and if their sum $= T$, then the rate equation is given by

$$-\frac{d[T]}{dt} = k_0[Co(NH_3)_5(C_2O_4)^+] + k_1[Co(NH_3)_5(C_2O_4)H^{2+}] + k_2[Co(NH_3)_5(C_2O_4)H^{2+}][H^+] \qquad (55)$$

The rate constant k_0 was determined in solutions of low acidity and as K_a had been evaluated the relative concentrations of protonated and non-protonated forms could be calculated.

Andrade and Taube pointed out the remarkable similarity between the parameters evaluated by different workers[50,78], for the two complex ions $[Co(NH_3)_5(C_2O_4)H]^{2+}$ and $[Co(NH_3)_5OOC.CF_3]^{2+}$ (see Table 13). In their view this demonstrates that the hydrogen oxalato complex does not avail itself of the opportunity it has for redistributing the proton in the activated complex, i.e.

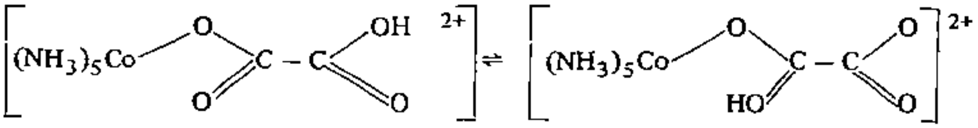


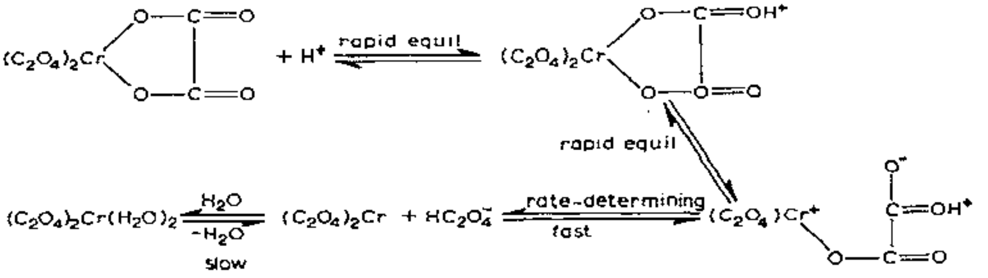
TABLE 13

Activation parameters and rate constants

Parameter	$\Delta S^{\ddagger}$ (cal.deg^{-1}.mole^{-1})	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	10^5k_1 (sec^{-1})	10^5k_2 (mole^{-1}.sec^{-1})
$Co(NH_3)_5(C_2O_4)H^{2+}$	1	28	1.5	2.8
$Co(NH_3)_5OOC.CF_3{}^{2+}$	−2	26	5.7	3

This being so, it is less remarkable that k_0 and k_1 (eqn. (55)) are so nearly alike for the oxalato complex ($10^8 k_0 = 1.5\ \text{sec}^{-1}$ and $10^8 k_1 = 2.2\ \text{sec}^{-1}$).

Many studies concerning the hydrolysis of trioxalato complexes have been reported. The hydrolyses of $\text{Co(oxalato)}_3{}^{3-}$ and $\text{Cr(oxalato)}_3{}^{3-}$ have been studied over a wide range of acid concentration using different acids[79]. For a given acid concentration, or a given value of the acidity function, the rate constant depends on the particular acid used. Above ca. 1 *M* acid the apparent reaction order with respect to acid concentration rises from ca. 1 to 3.5 (chromium complex) and to ca. 9 (cobalt complex). There is a linear relationship between $\log k_{\text{obs}}$ and acidity function, the slopes of the plots are approximately unity. Bunton et al. use this as evidence for a unimolecular mechanism, i.e. a dissociation of the protonated complex, water not being involved in the rate-determining step. The rate of reaction is greater in deuterium oxide than in water, indicating that a rapid pre-equilibrium is involved. (Deutero-acids generally have lower dissociation constants than the protium analogues, hence a higher concentration of conjugate acid is present in the deutero case.) The difference in the measured activation energies, i.e. 30.3 kcal.mole^{-1} for the cobalt complex; 24.4 kcal.mole^{-1} for the chromium case, were cited as evidence that the rate-determining step involves the metal atom, i.e. metal–oxygen bond fission as opposed to acyl–oxygen bond breaking. Bunton et al.[79] explained these results on the basis of the following mechanism (scheme 17).



Scheme 17.

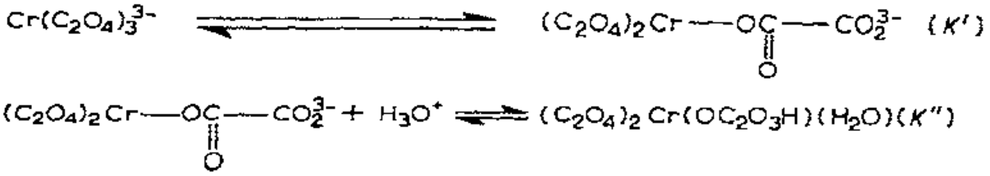
Kelm and Harris[80] point out that their results, for the $\text{Cr(oxalato)}_3{}^{3-}$ ion, fit the equation

$$k_{\text{obs}} = k_1 [\text{H}_2\text{O}^+] + k_2 [\text{H}_3\text{O}^+]^2 \tag{56}$$

and their interpretation differs somewhat from that of Bunton et al. They prefer a mechanism in which the sixth coordination position of the dechelated protonated substrate is occupied by a water molecule. It is argued that the effect of inert salts on the rate of hydrolysis favours a dual mechanism, i.e. one in which either a water molecule or H_3O^+ may attack the initially protonated substrate. The kinetic behaviour of the complex in solutions with, and without, added salts was compared. In perchloric acid (0.1 *M*) the rate constant is decreased by a factor of more than two as the ionic strength increases from 0.1 to 1.0, but little further change in k_{obs} occurs as the ionic strength is further increased.

Kelm and Harris[81] also studied the behaviour of the Cr(oxalato)$_3^{3-}$ ion at low acid concentration (pH ~ 2.6). Under these conditions the aquation anation equilibrium may be observed. The results of this study proved very useful and informative for the elucidation of the reactions at higher acid concentrations.

In a later paper Kelm and Harris[81] proposed that the pre-equilibrium was a combination of two steps, viz.



$$Cr(C_2O_4)_3^{3-} \rightleftharpoons (C_2O_4)_2Cr{-}O\underset{\underset{O}{\|}}{C}{-}CO_2^{3-} \quad (K')$$

$$(C_2O_4)_2Cr{-}O\underset{\underset{O}{\|}}{C}{-}CO_2^{3-} + H_3O^+ \rightleftharpoons (C_2O_4)_2Cr(OC_2O_3H)(H_2O)(K'')$$

Scheme 18.

The equilibrium constant, *K*, for the overall process is given by $K = K'K''$. *K* was estimated to be ~5 × 10^{-2} and as K'' ~10^2 then K' is only ~5 × 10^{-4}. Kelm and Harris pointed out, therefore, that it is unlikely that water occupies the sixth octahedral position[82] and he proposed a mechanism similar to Bunton's, although the steps occur in a different order.

Banerjea and Mohan[83–85] have also made a study of oxalato and malonato complexes. For the ion Cr(oxalato)$_3^{3-}$ their results and interpretations follow those of Kelm and Harris. The hydrolyses of the ions *cis*-Cr(oxalato)$_2$(H$_2$O)$_2^-$, *cis*-Cr(malonato)$_2$(H$_2$O)$_2^-$ have been compared[84,85]. The malonato complex reacts seventy times faster than the oxalato analogue ([H$^+$] = 1.0 *M*, 45°C). The greater lability of the malonato complex is attributed to the greater basicity of the malonato ligand which leads to a more favourable position of the pre-equilibrium protonation. Dissociation is also favoured by the lower thermodynamic stability of the malonato complex. Banerjea and Mohan explain the results in terms of a mechanism involving "solvent assisted dissociation" of the protonated substrate and prefer a mechanism in which the sixth coordination position is occupied by water.

The hydrolysis of [Cr(H$_2$O)$_4$ malonato]$^+$ ion has been reported[86]. The results were analysed using the Bunnett treatment. Banerjea and Chaudhuri conclude that the mechanism changes with the acid concentration, i.e. (1) when [HClO$_4$] = 1.5 to 3.0 *M* the mechanism is S$_N$1CA; (2) between 3.5 and 6.0 *M* [HClO$_4$] water is involved in the transition state; and (3) in 6.5 to 9.0 *M* HClO$_4$ water is involved as a proton transfer agent. This is rather a surprising conclusion. One might anticipate that water would be important in the transition state when it is present in a very large excess. However, the reverse appears to be postulated.

The rate of aquation of $[Rh(oxalato)_3]^{3-}$ ion[87] follows acidity function, not $[H^+]$ and/or $[H^+]^2$. This suggests that water is not involved in the transition state. Kinetic studies of this particular complex are complicated, however, by the ease of aquation of the complex even in the solid state. Harris and coworkers[88] [redacted] pointed out that an aqueous solution of $Rh(oxalato)_3{}^{3-}$ probably contains an appreciable proportion of the aquated species, since an NMR study has shown that even in the solid hydrate $K_3Rh(oxalato)_3 \cdot 4.5H_2O$, half the $Rh(oxalato)_3{}^{3-}$ ions are monoaquated. Harris and coworkers postulated a mechanism in which the first step is attack by H_3O^+ to give the conjugate acid in which the sixth coordination position is occupied by water, followed by loss of $HC_2O_4{}^-$ ion. Although a dissociative mechanism fits the above facts it is not supported by the high energy of activation (i.e. 5 kcal.mole^{-1} higher than that for the chromium analogue). A further difference between the rhodium and chromium complexes is the acid dependence i.e. first-order for rhodium, first- and second-order for chromium[89]. The rate of aquation of the rhodium complex is unaffected by the addition of sodium perchlorate.

There have been several studies concerned with complexes of chromium which also contain amine ligands. Contrary to the behaviour of the analogous cobalt or rhodium compounds, the amine ligands are replaced much more readily than the oxalato group. This is the case for α-$Cr(trien)(C_2O_4)^+$ which yields $Cr(H_2O)_4(C_2O_4)^+$ after one month at room temperature[90] and $Cr(en)(C_2O_4)_2{}^-$ which yields $Cr(H_2O)_2(C_2O_4)_2{}^-$. The release of amine ligands prior to, or parallel with, the hydrolysis of acido ligands is a common feature of chromium(III) chemistry.

The complex ion $Co(en)_2(C_2O_4)^+$ is stable in solutions of strong acids[91] (1.0 *M*) at 90°.

It is interesting to note that in the earlier literature there has been a conflict of views regarding the acid-catalysed exchange of oxygen atoms of oxalato groups coordinated to cobalt(III). Broomhead et al.[92] reported that only six of the twelve oxygen atoms exchanged whereas Llewellyn et al.[93] say that all twelve oxygen atoms exchange indistinguishably. This conflict has now been resolved[94]. All twelve oxygen atoms do exchange but there are two kinetically distinguishable groups, i.e. the six outer (carbonyl) oxygen atoms which exchange faster than the six inner (carboxyl) oxygen atoms. The experimental results obtained depend on the temperature used; at 45°C the rates of exchange are the same whereas at 25°C the carboxyl oxygen exchange is slow enough to be regarded as negligible and exchange does not proceed beyond fifty percent. The activation energies for the aquation or anation reactions are similar to that for inner oxygen atom exchange (42 ± 5 kcal.mole^{-1}) whereas the activation energy for outer oxygen atom exchange (17.2 kcal.mole^{-1}) is similar to that for the exchange in the case of free oxalic acid (18 kcal.mole^{-1}). The inner oxygen atom exchange is due to anation; the rate depends on the concentration of free oxalate ions. Furthermore the rates of anation and exchange of carboxyl oxygen atoms are approximately equal. A comparison of the aquations of $[Cr(malonato)_3]^{3-}$ and $[Cr(methylmalonato)_3]^{3-}$ ions has been reported[95]. The order of rate constants, viz. $Cr(Me(mal))_3{}^{3-} > Cr(mal)_3{}^{3-} > Cr(ox)_3{}^{3-}$, parallels the order of base strengths of the uncoordinated anions.

(xi) Carbamato complexes[96, 97]

The protonation of carbamato ligand has been studied.

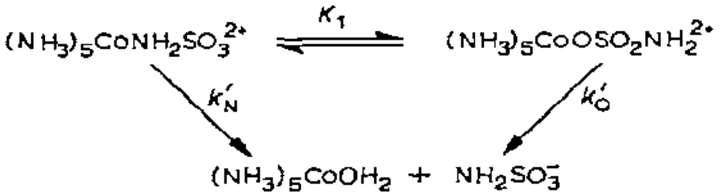
$$(NH_3)_5CoOOCNH_3^+ \overset{K_a}{\rightleftharpoons} (NH_3)_5CoOOCNH_2 + H^+$$

(K_a = 0.105 mole^{-1}; I = 1.0; 25.8°C)

The amine protons did not exchange with D_2O in neutral or basic solution but the exchange is catalysed by acid.

(xii) Sulphamato complexes[98]

The sulphamatopentamminecobalt(III) ion hydrolyses in acid solution. Although the product is the aquo complex, a detailed kinetic study suggests that the first stage is nitrogen–sulphur bond isomerism followed by subsequent, parallel hydrolysis (i.e. scheme 19)



Scheme 19.

(xiii) Nitrogen complexes

The reaction between various complexes of molecular nitrogen viz. [$CoH(PPh_3)_2N_2$], [$Co(PPh_3)_3N_2$] *trans*-[$Ir(PPh_3)_2N_2Cl$] and [$Ru(NH_3)_5N_2$]X_2 and strong acids has been studied quantitatively[99]. However, the products did not contain any ammonium salts. The metal was oxidised by the acid with the evolution of nitrogen and, often, hydrogen.

(xiv) Cyanato complexes

The acid-catalysed hydrolysis of the ion [$Co(NH_3)_5NCO$]$^{2+}$ is interesting since it proceeds without metal–ligand bond fission. The product is hexamminecobalt(III) ion[100].

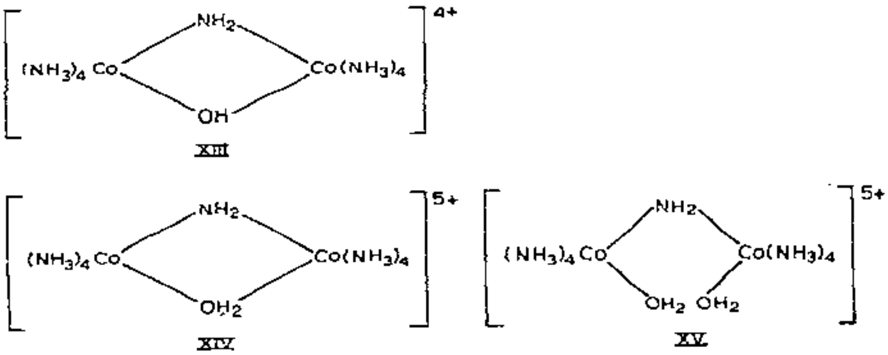
(xv) Perrhenato complexes[101]

The complex ion $[Co(NH_3)_5ReO_4]^{2+}$ is hydrolysed in aqueous solutions and the observed rate constant is given by eqn. (57). In dilute solutions of acid experiments involving the use of ^{18}O-oxygen show that a rhenium—oxygen bond is broken as opposed to a cobalt—oxygen linkage. However, in neutral solutions (pH 4 to 7) a more complicated oxygen transfer occurs. The hydrolysis is strongly catalysed by acetic acid, acetate ions and hydrogen phthalate ions.

$$\text{Rate} = (k_0 + k_\text{H}[\text{H}^+] + k_\text{OH}[\text{OH}^-])\,[\text{complex}] \qquad (57)$$

(xvi) Binuclear complexes

The hydrolysis of the binuclear complex ion XIII resulting in ring opening has been reported. The first step is always protonation of the μ-hydroxo group to yield the corresponding aquo (XIV) or diaquo species (XV)[102]. The subsequent anations have been extensively studied[103] and provide useful preparative routes[102–104]. Anation is effected by either mineral acid or a mixture of perchloric acid and a salt of the anating ion, e.g. potassium thiocyanate[103].



Scheme 19.

Reactions involving analogous μ-amido-μ-peroxo complexes also involve rapid, reversible protonations[105].

As there is already an extensive review[105] on the chemistry of these binuclear complexes their reactions will not be discussed further.

C. SQUARE PLANAR COMPLEXES

(i) Hydrido complexes

The complex *trans*-[Pt(PEt$_3$)$_2$Cl.H] is insoluble in water. If, however, it is suspended while molten (ca. 80°C), in hot aqueous solution, the hydrido ligand exchanges rapidly with deuterium oxide if small amounts of acid are present[106]. These qualitative observations were extended by Falk and Halpern[107]. The kinetics of the exchange reaction (scheme 20) in D$_2$O–acetone solvent were studied. This reaction is very slow in the absence of acid ($10^5k \sim 1.0$ sec^{-1}) but is accelerated by DClO$_4$ and even more markedly by DCl.

(a) In 25% D$_2$O–75% acetone

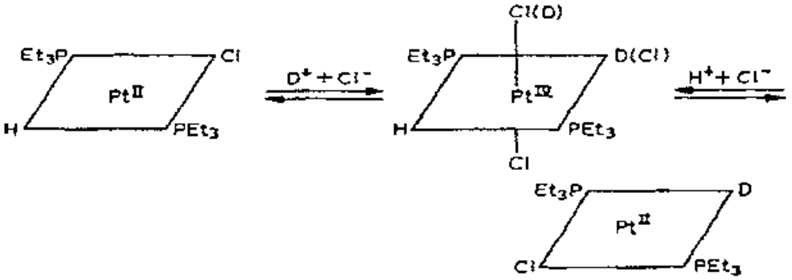
$$\text{Rate} = (k_1 + k_2[\text{Cl}^-])\,[\text{D}^+][\text{Pt(PEt}_3)_2\text{Cl.H}] \qquad (58)$$

where $10^2k_1 = 4.1$ l.mole^{-1}.sec^{-1} and $k_2 = 6.0$ l^2.mole^{-2} (30°C)

The rates of both the chloride ion-dependent and independent pathways show an inverse dependence on D$_2$O content in the solvent mixture.

(b) In 10% D$_2$O–90% acetone, the rates of both pathways remain first-order in [D$^+$], whereas the apparent reaction order with respect to [Cl$^-$] for the chloride-dependent pathway became 1.4. In this solvent mixture, $10^2k_1 = 7.3$ l.mole^{-1}.sec^{-1} and $k_2 =$ 36 l$^{2.4}$.mole$^{-2.4}$.sec^{-1}.

The catalysis is explained in terms of a mechanism involving protonation of the platinum atom (scheme 20).



Scheme 20.

A compound, [Pt(PEt$_3$)$_2$H$_2$Cl$_2$], similar to the postulated intermediate, has been prepared. The proposed mechanism also predicted that chloride exchange should also occur. Experiments using ^{36}Cl$^-$ ion revealed that chloride exchange occurs much more rapidly than hydrogen exchange, apparently by a direct method which does not involve acid catalysis.

(ii) Alkyl and aryl complexes

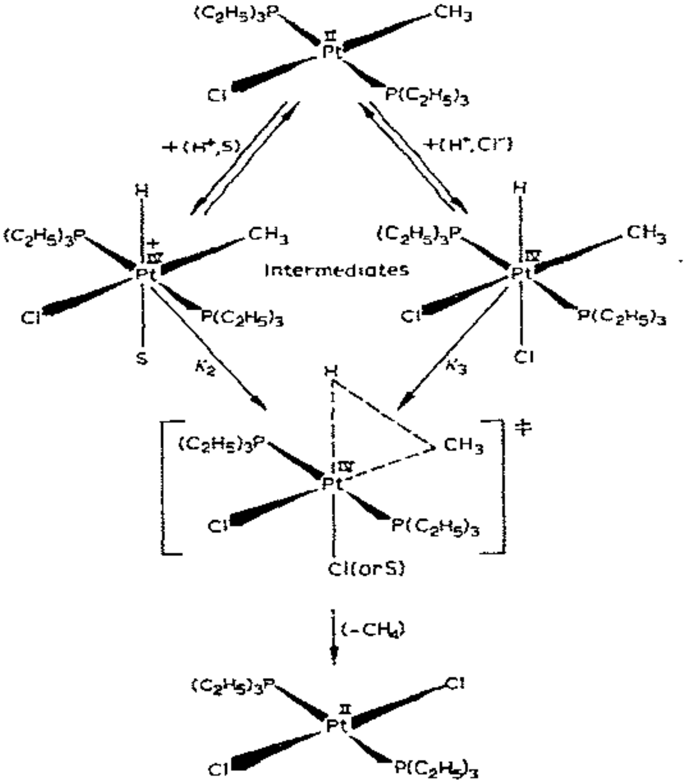
A methanolic solution of *trans*-$[Pt(PEt_3)_2CH_3.Cl]$ reacts with hydrochloric acid to yield *trans*-$[Pt(PEt_3)_2Cl_2]$ and methane[108], i.e. eqn. (59).

$$\textit{trans}\text{-}[Pt(PEt_3)_2CH_3.Cl] + H^+ + Cl^- \longrightarrow \textit{trans}\text{-}[Pt(PEt_3)_2Cl_2] + CH_4 \qquad (59)$$

The reaction obeys the rate law

$$\text{Rate} = (k_2 + k_3[Cl^-])\,[H^+]\,[\text{complex}] \qquad (60)$$

The rate of reaction of the analogous compound *trans*-$[Pt(PEt_3)_2CH_3I]$ to yield the chloroiodo complex, is independent of the chloride ion concentration. It was not possible to study the effect of iodide ions because oxidation to iodine occurred under the relevant experimental conditions. The proposed mechanism for these reactions is shown in scheme 21.



Scheme 21.

A methanolic solution of *trans*-[$Pt(PEt_3)_2(C_6H_5)_2$] reacts with acids in the presence of chloride ions to yield *trans*-[$Pt(PEt_3)_2C_6H_5.Cl$] and benzene[109]. No reaction occurs with lithium chloride in the absence of acids. The rate law observed for the reaction is

$$\text{Rate} = k[\text{complex}][\text{H}^+] \qquad (61)$$

In marked contrast to the alkyl case (above) there is no evidence for a pathway involving anions, A^-, since the reaction rate is independent of anion concentration. The proposed mechanism is similar to scheme 21.

(iii) Nitro complexes

Complexes of the series *cis*- or *trans*-$PtA_2(NO_2)_2$ (where A = NH_3, pyridine, SEt_2, PEt_3 or thiourea) react with aqueous sulphuric acid, the nitro groups being successively replaced[110,111]. The rate of replacement of the nitro groups is acidity function dependent, i.e. $\log k_{\text{obs}}$ vs. $-H_0$ is a straight line of approximately unit slope. This suggests that solvent molecules do not participate in the rate-determining step. The most likely mechanism is an intramolecular breakdown of the protonated complex to yield a nitrosonium ion and a transient hydroxo species, similar to scheme 6. There is an alternative possibility, i.e. a mechanism similar to scheme 21. However, attempts to observe a proton resonance, at high fields due to a proton bonded directly to a platinum atom, were unsuccessful. The rates of replacement of the nitro ligand from these complexes in acetic acid as solvent have also been studied. The results are of the same general form as for the aqueous system[113].

The rate of release of nitro ligand from $Pt(NO_2)_4{}^{2-}$ and $PtCl_3NO_2^{2-}$ ions in different acids has been studied[112]. For the ion $Pt(NO_2)_4{}^{2-}$, no maximum rate constants were observed, the rate constants being acidity function dependent.

The hydrolysis of nitro ligand from $PtCl_3NO_2{}^{2-}$ ion is relatively slow; maximum rate constants were observed[112]. The maximum rate constant in sulphuric acid is greater than the value for perchloric acid. This may be explained in terms of ion-pairing of bisulphate ion with the leaving nitrosonium ion.

D. CHELATE COMPOUNDS

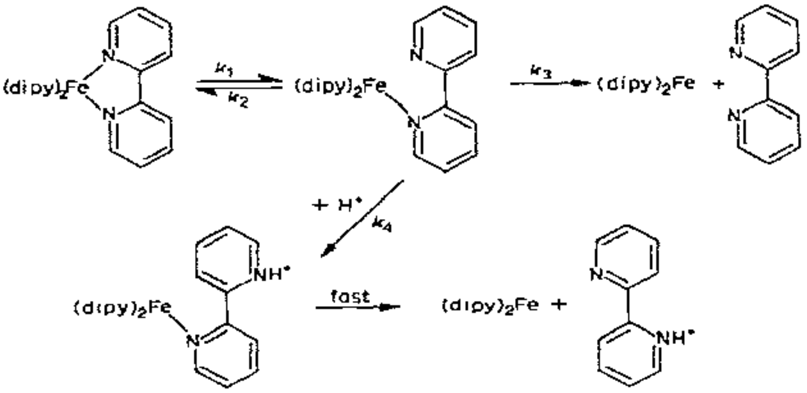
The hydrolysis of chelate complexes may be acid-catalysed. There are certain features, e.g. several metal—donor atom bonds, ring strain, which are specific to chelate compounds and may have a profound influence on rate and mechanism.

One of the earliest and most interesting cases is that of the [$Fe(dipy)_3$]$^{2+}$ ion. The hydrolysis is acid-catalysed but as the acid concentration increases beyond 2 *M* a limiting maximum rate constant is observed. Baxendale and George[114] explained this in terms of the equilibrium

$$\underset{\text{XVI}}{\text{Fe(dipy)}_3{}^{2+}} + \text{H}^+ \rightleftharpoons \underset{\text{XVII}}{\text{Fe(dipy)}_3\,\text{H}^{3+}} \qquad (62)$$

The results then require that XVII reacts faster than XVI, which is not unlikely. A limiting rate constant should be observed only when XVII is the sole species present.

Basolo et al.[115] and Murmann and Healy[116] have contested this interpretation. Basolo et al. point out that the spectra of the complex in neutral and acidic ($H^+ = 1.0\,M$) solutions are almost identical and that therefore very little of species XVII is present under conditions where catalysis is appreciable. It must be pointed that the spectra of species XVI and XVII need not necessarily be very different. Murmann and Healy claim to have characterised protonated forms of $[Fe(dipy)_3]^{2+}$ and its analogues; the protonations are accompanied by spectral and magnetic changes. This has been shown by Schilt[117] to be a redox process (see Section F). Basolo and Pearson have postulated the following reaction scheme 22.



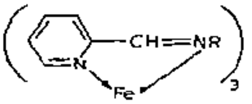
Scheme 22. Reproduced from refs. 41 and 115 by permission of the authors, the American Chemical Society and John Wiley and Sons, New York.

$$\text{Then } k_{\text{obs}} = k_1 \left(\frac{k_3 + k_4[H^+]}{k_2 + k_3 + k_4[H^+]} \right) \tag{63}$$

The qualitative behaviour of the acid dependence agrees with eqn. (63). From a knowledge of the two limiting rates, i.e. (1) in dilute acid $[H^+]$ negligible and (2) the maximum rate constant $[H^+]$ high, it was deduced that at low acid concentrations, each time a single Fe—N bond breaks it will reform 84% of the time and in the other 16% of the time the second Fe—N bond will break. The hydrolysis of the analogous $Fe(O\text{–}phen)_3^{2+}$ ion is not acid-catalysed[118, 119]; this finding supports Basolo's "flexible multidentate" mechanism.

A point of interest concerning mechanism 22 is that a metal M^+ may replace the proton H^+ as the electrophile in the first step, i.e. once one end of a chelate group is dissociated from the metal ion it may bond to either H^+ or M^+. In some systems, e.g. EDTA complexes (see below), competition between these two pathways may be observed.

Murmann and Healy[120] also made a neat attempt to elucidate hydrolysis mechanisms of chelated complexes by using a careful choice of donor groups. They chose as substrate the Schiff base complex tris(pyridinalalkylimine) iron(II) perchlorate (scheme 23)



Scheme 23.

for the following reasons. If the Schiff base gave rise to a half-bonded structure, the $-CH{=}NR$ grouping would be rapidly hydrolysed and this might modify the $[H^+]$ dependence of the rate constants. The hydrolysis of the half-bonded Schiff base would be superimposed on the kinetics of the hydrolysis analogous to that of the dipyridyl complex. However, they found that complete dissociation preceded hydrolysis of the Schiff base. The acid dependence parallels that of $[Fe(dipy)_3]^{2+}$ ion. The size and geometry of the alkyl group does affect the magnitude of the rate constants but leaves the general kinetic pattern unaltered.

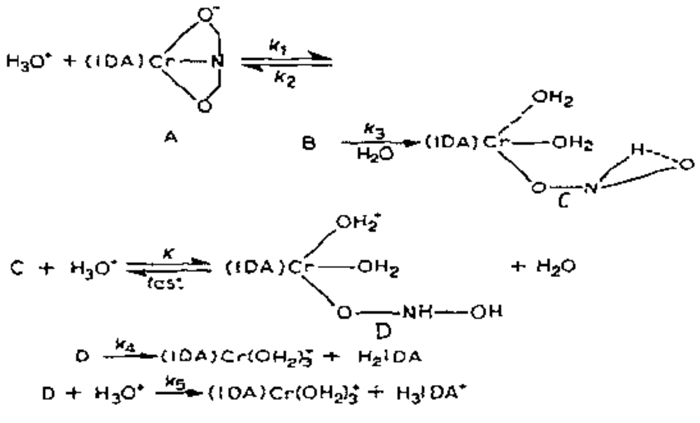
The mechanism of the acid dissociation of the Schiff base complexes appears to be of the same type as that previously observed for $Fe(dipy)_3{}^{2+}$. The rate expression, acid dependence, salt effects and temperature dependence are about the same for the two systems. If the mechanism of hydrolysis of $Fe(PrPI)_3{}^{2+}$ ion included, as a rate-determining step, the hydrolysis of the chelated ligand, the kinetics would not be similar to those for $Fe(dipy)_3{}^{2+}$ ion where hydrolysis of the ligand cannot occur. The "half-bonded" intermediate suggested in reaction scheme 22 is less plausible for iron complexes of Schiff bases. With one end of the ligand unattached, there would be a strong tendency for hydrolysis of the $-C{=}N-$ linkage in the ligand with resultant modification of the acid dependence. Several Schiff bases were used but no cases involving modified acid dependence were found. There are many mechanisms which give rise to the observed kinetic equation using the half-bonded, the protonated or other intermediates. In the case of these Schiff base complexes, Murmann and Healy indicate that their observations could be justified on the basis of the protonated species concept of Baxendale and George. They postulated that the interaction with acid was not localised around the nitrogen donor atoms but was concerned with the aromatic portion of the ligand and that such interaction could explain the spectral and magnetic changes which they observed on protonation. Tobe and coworkers also report that there is no significant change in the spectrum of $Fe(o\text{-phen})_3{}^{3+}$ ion when the solvent is changed from water to 98% sulphuric acid. The rate of hydrolysis of $Fe(o\text{-phen})_3{}^{3+}$ in concentrated sulphuric acid is very slow but increases markedly as the acid concentration decreases[121], i.e. as the water concentration increases. However, a plot of $\log k_{obs}$ vs. $\log a_{H_2O}$ does not have unit slope. Tobe and coworkers[121] forward these results as evidence for a bimolecular (or possibly higher molecularity) reaction, i.e. they postulated that partial binding of water to the metal in the transition state is essential.

Farina et al.[122] compared the kinetic behaviour of $M(dipy)_3^{2+}$ and $M(terpy)_2^{2+}$ ions (where M = Co, Ni or Fe). The rate constant for the rupture of a pyridine nitrogen–metal bond is only slightly smaller when it is part of a single (dipy) ring system than when it forms part of a double ring (terpy) system. The kinetic scheme postulated was similar to scheme 22.

The aquation of iminodiacetato complexes is acid-catalysed[123]. In acidic solutions ($[H^+] = 0.1-1.0\,M$) *cis*-bisiminodiacetatochromate(III) ion undergoes partial aquation to yield triaquoiminodiacetatochromate(III) ion. The product aquates further only at an extremely slow rate under these conditions. Although the overall reaction may be as described in the foregoing sentences, it is not an accurate description because the first-order plots for any given run ($[H^+] \gg$ [complex]) are not linear until the later stages of the reaction. This suggests some consecutive-step mechanism, e.g.

$$cis\text{-}Cr(IDA)_2^- \xrightarrow{k'_1} I \xrightarrow{k'_2} Cr(IDA)(H_2O)_3^+ \tag{64}$$

The two rate constants k'_1 and k'_2 were named the fast and slow rates of aquation by Weyh and Hamm[123]. The experimental data showed that the "fast" rate constant is first-order in hydrogen ion concentration, i.e. $k_f = k'[H_3O^+]$, and that the "slow" rate constant is given by $k_s = k'' + k'''[H_3O^+]$. The effect of ionic strength was studied; k_f decreases with increasing ionic strength whilst the reverse is true for k_s. The proposed mechanism which fits all the experimental data is given in scheme 24.



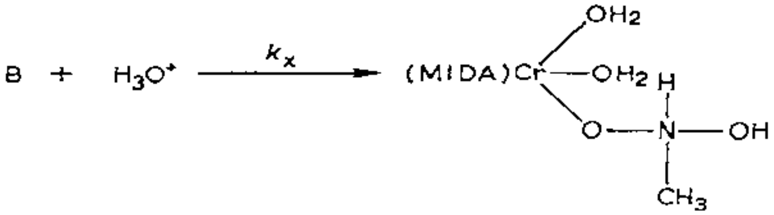
Scheme 24.

Ion-exchange experiments showed that the intermediate had a charge of +1 and it was postulated that it contained one tridentate iminodiacetato ligand and one bidentate one.

The complex ion *trans*-(*fac*)-bis(methyliminodiacetato)-chromate (III) ion is also partially aquated in acidic solutions ($[H^+] = 0.1-1.0\,M$), losing one of the tridentate ligands. However, in this case, the pseudo-first-order rate constant plots were linear, indicating that only one step was being observed. The observed first-order rate constant is given by

$$k_{obs} = (k'[H_3O^+] + k''[H_3O^+]^2)[Cr(MIDA)_2^-] \qquad (65)$$

The mechanism is similar to that for *cis*-$[Cr(IDA)_2]^-$ ion but involves the additional step



(D)

(66)

The activation parameters for these reactions are collected in Table 14.

There have been many studies of so-called "multidentate ligand kinetics". These involve a kinetic study of the dissociation and/or formation of polydentate metal complexes and the order in which the several donor atoms concerned dissociate from the metal ion. In some cases attempts have then been made to correlate the kinetic data with the relative stability constants for all the metal—ligand bonds concerned.

Metal exchange reactions of ethylenediaminetetraacetato ion (Y^{4-} or EDTA) have been the subject of considerable interest. The general reaction may be written[124–128]

$$M_1^{2+} + M_2(Y^{2-}) \rightleftharpoons M_1(Y^{2-}) + M_2^{2+} \qquad (67)$$

(where M_1^{2+} and M_2^{2+} are different metal ions or two different isotopes of, for example, nickel ion). In some of these metal exchange reactions an acid-catalysed path may compete with the pathway involving the more direct ligand transfer reaction. Isotopic exchange reactions have been investigated and will be discussed first.

The rate of exchange between ethylenediaminetetraacetato—iron(III) and ferric ions is acid-catalysed[129]. The overall rate equation is given by

TABLE 14

Activation parameters for the acid-catalysed hydrolysis of some iminodiacetato complexes

Complex	Step concerned	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal.deg^{-1}.mole^{-1})
cis-$[Cr(IDA)_2]^-$	k'	15.3	−17.0
	k''	17.0	−18.7
	k'''	24.3	− 5.1
trans-$[Cr(MIDA)_2]^-$	k'	17.0	−18.6
	k''	15.6	−21.2

$$\text{Rate} = k_1[\text{FeY}^-][\text{H}^+]^3 + k_2[\text{FeY}^-][\text{Fe}^{3+}] + k_3[\text{FeY}^-][\text{Fe}^{3+}]/[\text{H}^+] \tag{68}$$

although there is some doubt about the order with respect to $[\text{H}^+]$ in the second term. At relatively high acidity (0.1–0.31 *M*; *I* = 0.48–1.10) the mechanism may be written as eqns. (69) and (70)

$$\text{Fe(Y}^-) + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{Fe(Y}^+)\ (\text{equilibrium}) \tag{69}$$

$$\text{H}_2\text{Fe(Y}^+)\text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{H}_3(\text{Y}^-)\ (\text{rate-determining}) \tag{70}$$

The second and third terms of eqn. (68) correspond to the slow steps

$$\text{FeY}^- + {}^*\text{Fe}^{3+} \longrightarrow {}^*\text{FeY}^- + \text{Fe}^{3+}\ (\text{slow})\ \text{and} \tag{71}$$

$$\text{FeY}^- + {}^*\text{FeOH}^{2+} \longrightarrow {}^*\text{FeY}^- + \text{FeOH}^{2+}\ (\text{slow}) \tag{72}$$

The second and third terms of the rate equation are subject to large negative salt effects whilst the first term shows no salt effect whatsoever.

Cook and Long[130] have studied the rate of radionickel exchange with Ni(EDTA)^{2-} ion. All the experimental data fit the rate equation

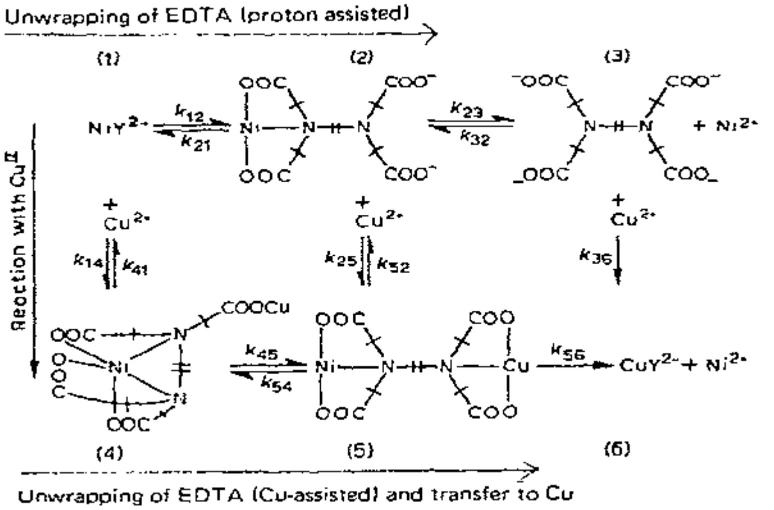
$$\begin{aligned}\text{Rate} = {} & k_1[\text{Ni}^{2+}][\text{NiY}^{2-}] + k_2[\text{H}^+][\text{Ni}^{2+}][\text{NiY}^{2-}] + k_3[\text{H}^+][\text{NiY}^{2-}] \\ & + k_4[\text{H}^+]^2[\text{NiY}^{2-}] + k_5[\text{H}^+]^3[\text{NiY}^{2-}]\end{aligned} \tag{73}$$

The proposed mechanism (scheme 15) involves a series of rapidly established preliminary equilibria between protons and NiY^{2-} followed by unimolecular dissociation steps or collisions with nickel(II) ions.

$$\begin{array}{lcll}
\text{Ni}^{2+} + {}^*\text{NiY}^{2-} & \rightleftharpoons & {}^*\text{Ni}^{2+} + \text{NiY}^{2-} & (\text{slow}) \\
\text{H}^+ + {}^*\text{NiY}^{2-} & \rightleftharpoons & \text{HNiY}^- & (\text{equilibrium}) \\
\text{H}^*\text{NiY} & \rightleftharpoons & {}^*\text{Ni}^{2+} + \text{HY}^{3-} & (\text{slow}) \\
\text{Ni}^{2+} + \text{H}^*\text{NiY} & \rightleftharpoons & {}^*\text{Ni}^{2+} + \text{HNiY}^- & (\text{slow}) \\
\text{H}^+ + \text{H}^*\text{NiY} & \rightleftharpoons & \text{H}_2{}^*\text{NiY} & (\text{equilibrium}) \\
\text{H}_2{}^*\text{NiY} & \rightleftharpoons & {}^*\text{Ni}^{2+} + \text{H}_2\text{Y}^{2-} & (\text{slow}) \\
\text{Ni}^{2+} + \text{H}_2{}^*\text{NiY} & \rightleftharpoons & {}^*\text{Ni}^{2+} + \text{H}_2\text{NiY} & (\text{slow}) \\
\text{H}^+ + \text{H}_2{}^*\text{NiY} & \rightleftharpoons & \text{H}_3{}^*\text{NiY}^+ & (\text{equilibrium}) \\
\text{H}_3{}^*\text{NiY}^+ & \rightleftharpoons & {}^*\text{Ni}^{2+} + \text{H}_3\text{Y}^- & (\text{slow})
\end{array}$$

Scheme 25.

The exchange of copper(II) ion and ethylenediaminetetraacetatonickel(II) ion has been studied[131] and the overall reaction scheme (scheme 26) may be written



Scheme 26. Stepwise unwrapping of EDTA from its nickel complex and the formation of the copper-EDTA complex. Only species 1,4,6 and protonated forms of 3 are observable intermediates. Species 2 and 5 are proposed reaction intermediates. Reproduced from ref. 131 by permission of the authors and the American Chemical Society.

The dependence of the rate on the concentrations of copper(II) ions and hydrogen ions was studied very carefully. For reactions involving a large excess of copper(II) ion, k_0 may or may not vary with this excess concentration and the rate is given by

$$\text{Rate} = k_0[\text{NiY}_\text{T}] \tag{74}$$

(where $[\text{NiY}_\text{T}]$ refers to the total of all forms of Ni(EDTA), i.e. $[\text{NiY}_\text{T}] = [\text{NiY}] + [\text{NiHY}^-] + [\text{NiH}_2\text{Y}] + [\text{NiYCu}]$). Some reactions were studied at low concentrations without excess copper(II) ion, giving a second-order rate constant k and

$$\text{Rate} = k[\text{NiY}_\text{T}][\text{Cu}_\text{T}] - k'[\text{CuY}_\text{T}][\text{Ni}_\text{T}] \tag{75}$$

The EDTA may dissociate completely from its metal complex before reacting with another metal. This occurs at high acidity and low concentration of reacting metal. In the case of Ni(EDTA)^{2-}, acid catalyses the complete dissociation with the rate expression

$$\text{Rate} = k_1[\text{H}^+][\text{NiY}^{2-}] + k_2[\text{H}^+][\text{NiYH}^-] + k_3[\text{H}^+]^2[\text{NiYH}^-] + k_4[\text{H}^+]^3[\text{NiYH}^-] \tag{76}$$

Thus at high acidity, step 1,2,3,6 in scheme 26 occurs before copper(II) reacts with EDTA and this rate of dissociation reaches a maximum at 0.7 *M* hydrochloric acid. However at pH ⩾ 2 the complete dissociation step (1,2,3,6) does not contribute to the overall reaction and two pathways remain. One of these involves the proton assisted half dissociation of NiY^{2-}, i.e. the unfolding of one iminodiacetato segment from nickel ion. It was also demonstrated that hydrogen ion is much more effective than copper ion in assisting the half opening of EDTA from nickel. Even after NiYCu has formed it is only one-seventh as effective as $NiYH$[illegible] in causing the "half opening" of EDTA. The NiYCu (or $NiYH^-$) species are formed by attachment of copper ion to an oxygen atom of EDTA. The formation is far too rapid to be accounted for by an attachment to a nitrogen atom.

Although in an earlier paper[132] a narrower range of reactant concentrations was used, it was possible to show how the rate constants for copper(II) and radionickel(II) ions differed in their acid dependence. The results are summarised in Table 15 and show quite clearly the acid catalysis for the nickel exchange reaction. Bydalek and Margerum pointed out that care must be taken to consider the complete stepwise mechanisms when extrapolating rate data from one concentration range to another.

The importance of steric effects in these multidentate ligand reactions has been demonstrated. The complex *trans*-cyclohexylenediaminetetraacetatonickel(II) does not exchange with copper(II) ion[133]. However, the dissociation is very pH-dependent. The hydrocarbon part of the polydentate ligand prevents complex formation by the copper ion but not by the proton. This has been explained with the aid of molecular models (Fig. 3).

The dissociation of mono-*cis, cis*-1,3,5-triaminocyclohexanenickel(II) ion is extraordinarily slow compared with other related but less sterically restricted nickel(II) complexes[134], e.g. $Ni(dien)^{2+}$. In 5 *M* nitric acid the former dissociates with a half life of 7 min whereas the latter dissociates "instantaneously". The rate law (63) is obeyed and the results were interpreted in terms of scheme 27. The actual stereochemistry is important when possible mechanisms are considered[134, 135]. Breakage of the first Ni–N necessarily forces one of the remaining six membered rings into an unstable boat ion formation. The conformation change in XVIII was achieved by rotation within the cyclohexane ring across a potential barrier which should be ca. 10 kcal.mole^{-1}. The triaxial conformation of the ring is retained in XIX but a conformational change has occurred within the metal-containing ring. The potential barrier of this process is unknown, thus we cannot decide between XVIII and XIX, as both contain non-bonded contacts which should cause either of them to be very unstable. The relatively slow rate of hydrolysis was explained in terms of a very unfavourable pre-equilibrium (scheme 28).

TABLE 15

Second-order rate constants for the reaction $NiY_T + M^{2+}$. Reproduced from ref. 132 by permission of the authors and the American Chemical Society.

$NiY_T^{\cdot}$ species	Second-order rate constant	Cu^{2+}	Ni^{2+}
NiY^{2-}	k_1	1.6×10^{-2}	8×10^{-7}
$HNiY^-$	k_2	1.6×10^{-2}	4×10^{-4}
H_2NiY	k_3	1.6×10^{-2}	5.6×10^{-3}

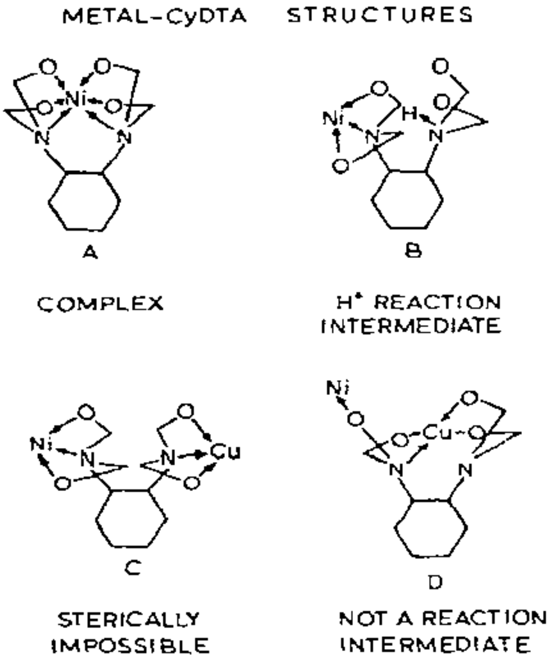
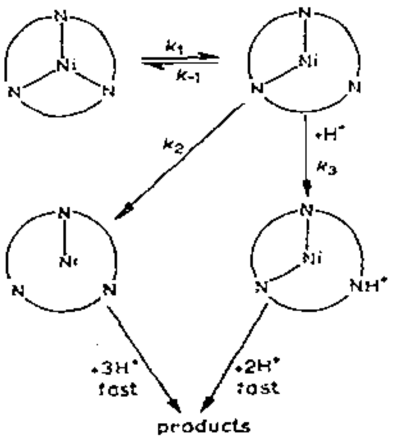
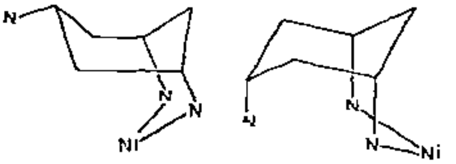


Fig. 3. Metal–CyDTA structures. A. One metal can coordinate both nitrogens to form the stable complex. B. An iminodiacetate segment bonded to the metal can be rotated but the remaining segment cannot accept another metal ion at the nitrogen. It can be protonated as shown. C. This structure is not possible due to steric hindrance of the acetate groups with one another and the ring. D. This structure is possible but cannot be a reaction intermediate for Cu^{2+} attack of $NiCy^{2-}$. Nor is there any evidence of an intermediate corresponding to a structure where Ni^{2+} and Cu^{2+} change places. Reproduced from ref. 134 by permission of the authors and the American Chemical Society.



Scheme 27.



XVIII XIX

Scheme 28.

The dissociation of Ni(penten)$^{2+}$, Ni(tetraen)$^{2+}$, Ni(dien)$^{2+}$ and Ni(en)$^{2+}$ complexes is acid-catalysed. Protonation of nitrogen donor atoms increases the concentrations of intermediate species, i.e. complexes in which at least one nickel–nitrogen bond has been broken. The formation of non-bonded structures containing unprotonated species is quite unfavourable. In one study[136] it was stated that the rate determining step appears to be the breaking of the last nickel–nitrogen bond.

Wilkins et al.[137] have been able to distinguish three steps in the mechanism of these reactions and have been able to measure the rate constant for more than one step. The complexes studied were Ni(N–pren)$^{2+}$, Ni(ptn)$^{2+}$, Ni(dien)$^{2+}$, Ni(dapa)$^{2+}$, Ni(tren)$^{2+}$, Ni(trien)$^{2+}$, Ni(penten)$^{2+}$. In all cases except that of Ni(en)$^{2+}$, the first Ni to NH_2 group bond is ruptured very rapidly. The second stage is slower by factors ranging from 4 to 200 for the different complexes. These differences do not appear to be associated with either the energies or entropies of activation. The last stage of the decomposition, when the metal is bonded to only one nitrogen atom, is again very fast and usually undetected by the stopped flow method. The energies of activation for the first nickel–nitrogen bond rupture fall neatly into two groups. The highest value is for the bidentate Ni(en)$^{2+}$ complex ($E \sim 21$ kcal.mole^{-1}) which is the most strain free chelate. For the tridentate complexes $E \sim 18$ kcal.mole^{-1} and only ca. 15 kcal.mole^{-1} for tetra- and penta-dentates. The entropy of activation likewise falls into two sets of values. The effect of ring size on the rate is relatively small. However, the accelerating effect of charge placed near the reacting donor centre is shown up by comparing the complexes of the isoelectronic ligands $NH_2{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}CH_3$ (N-pren) and $NH_2{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_3^+$. The latter reacts some nine times faster than the former. A study of unsymmetrically substituted diamines was also made and the relative contributions from Ni–NHR and Ni–NH_2 bond fissions were evaluated.

E. CRITERIA USED TO ASSIGN MECHANISMS TO ACID-CATALYSED REACTIONS FROM KINETIC DATA

There are two main concepts used by kineticists when attempting to elucidate mechanisms of acid-catalysed reactions from purely kinetic, as opposed to stereochemical and/or reaction product, data. The criteria are the two postulates, one the Zucker–Hammett hypothesis[138], the other due to Bunnett[139]. Both approaches concern the role of water in the rate-determining step, i.e. if water is not involved in the rate-determining step (or the transition state) then the reaction is designated as unimolecular.

The Zucker–Hammett postulate[138] may be summarised as follows. If a plot of the logarithm of the pseudo-first-order rate constant, log k, vs. Hammett acidity function is a straight line of unit slope then the reaction is unimolecular. On the other hand, if a plot of log k vs. the logarithm of the stoichiometric acid concentration is a straight line of unit slope, the reaction is bimolecular. Strictly, these relationships apply only to conditions which give rise to low degrees of protonation of the substrate. When the substrate is appreciably protonated more complicated relationships apply (see eqn. (9)).

The second approach is due to Bunnett[139], who pointed out that the Zucker–Hammett hypothesis has been misused. There is a tendency for researchers to choose between the two types of plot concerned; thus by forcing their kinetic data into one division, as opposed to the other, subtle differences in mechanism have been masked. Bunnett therefore postulated a new approach involving the activity of water. Plots of (log k + H_0) against logarithm of activity of water are drawn up and the slope of the plot (called the w value) is used as a criterion of mechanism as summarised in Table 16.

In some cases the plot corresponding to w is not linear. However, in such cases eqn. (77), or one of its more refined forms, applies. The parameter w^* may then be used as a useful criterion of mechanism (see Table 16).

$$\log k - \log C_{\text{acid}} = w^* \log a_w + \text{constant} \tag{77}$$

Later Kresge et al.[140] suggested an approach for assigning mechanisms which does not involve the use of Hammett's acidity function. The basis is that the activity coefficient of the transition state, $y^{\ddagger}$, can be represented by eqn. (80) in which α represents the degree to which the transition state resembles the conjugate acid. For the exchange reaction

$$H^1Ar + H^+ \rightleftharpoons H^1ArH^+ \rightleftharpoons H^{1+} + HAr \tag{78}$$

TABLE 16

Values of w and w^* characteristic of the way in which water is involved in the rate-determining step of acid-catalysed reactions for substrates protonated on oxygen or nitrogen

Involvement of water	w values	w^* values
Not involved	−2.5–0.0	
Nucleophile	1.2–3.3	−2[a]
Proton transfer agent	3.2	−2[a]

[a] This distinction is not an exact one.

The experimental rate constant is given by

$$k_1 = \frac{kC_{H^+}}{K_{SH^+}} \cdot \frac{y_{H^+} y_{HAr}}{y^{\ddagger}} \tag{79}$$

and

$$y^{\ddagger} = (y_{HA^+} \cdot y_{H^+})^{1-\alpha} \cdot y_{HArH^+}{}^{\alpha} \tag{80}$$

If $I = C_{HArH^+} / C_{HAr}$, then

$$\log(k_1 C_{H^+}) = \alpha \log (I/C_{H^+}) + \log (k K_{SH^+}{}^{\alpha-1}) \tag{81}$$

The parameter α may be determined from the slope of the graph of $\log (k/C_{H^+})$ against $\log (I/C_{H^+})$. This is not easily applicable to many inorganic systems because I is often not known.

F. APPROPRIATE ACIDITY FUNCTIONS AND INDICATOR RATIO MEASUREMENTS

The pH scale breaks down as a useful measure of acidity for solutions whose ionic strengths are greater than 0.1 *M*. Some other quantitative scale is, therefore, required for more concentrated solutions of strong acids. With this aim in view Hammett and Deyrup[141] in 1932 defined an "acidity function". They suggested that such a scale could be provided by the spectrophotometric determination of the extent of protonation of weakly basic indicators in acidic solutions. Considering a weak base B, the appropriate equilibrium is

$$B + H^+ \rightleftharpoons BH^+ \tag{82}$$

Hammett and Deyrup proposed an acidity function H_0 defined by eqn. (83)

$$H_0 = pK_{BH^+} - \log ([BH^+]/[B]) \tag{83}$$

where

$$pK_{BH^+} = -\log \left(a_{H^+} \cdot \frac{[B]\, y_B}{[BH^+]\, y_{BH^+}} \right) \tag{84}$$

and if

$$h_0 = a_{H^+} \cdot y_B / y_{BH^+}$$

then

$$H_0 = -\log h_0 = -\log (a_H + y_B / y_{BH^+}) \tag{85}$$

Hence H_0 will be independent of the particular indicator B used to measure it, provided that the ratio y_B/y_{BH^+} is identical for all bases in the same acid solution. This identity holds for structurally similar bases in a given acid solution. However, spectacular deviations occur when the structure of B is altered significantly. An excellent, more detailed survey and discussion of the acidity function concept has been made by Rochester[142].

When correlations between kinetic data and mechanisms are being attempted, a knowledge of the appropriate acidity function is desirable, if not essential. In some of the earlier studies of acido–ammine-type complexes, the H_0 acidity function was used for such correlations. This procedure has several drawbacks, viz., the transition metal complexes discussed in this survey are obviously very different chemically from the aniline-type indicators which Hammett used to set up the H_0 scale. It is well known[142] that the protonation of some organic molecules, e.g. 2-substituted pyridine oxides, azulenes, does not follow the H_0 scale. This may be described quantitatively by rewriting the equation as

$$H_0 = \mathrm{p}K_{\mathrm{BH}^+} - n(\log[\mathrm{BH}^+]/[\mathrm{B}]) \tag{86}$$

If a base is to be regarded as a Hammett indicator the value of n must be very close to unity. Furthermore H_0 applies to neutral bases whereas many transition metal complex substrates are positively charged. The H_+ scale has been less extensively studied than H_0. However, some measurements for aniline-type indicators of charge type B^+ in sulphuric and perchloric acid solutions have been studied. The results showed that for aniline-type molecules H_0 and H_+ were parallel[143].

These drawbacks show that the applicability of the H_0 scale to transition metal systems requires justification. This point is discussed in the following sections.

(i) Indicator ratio measurements

It has been shown that some isothiocyanato complexes are reversibly protonated in aqueous solutions of sulphuric acid and the protonations are accompanied by spectral changes. Thus indicator ratio measurements were possible[144] and the values of n (eqn. (86)) are given in Table 17. Although indicator ratios were determined and plots of log ($[\mathrm{BH}^+]/[\mathrm{B}]$) against (1) $-H_0$ and (2) some function of acid concentration, were constructed, actual values of an acidity function could not be evaluated because no $\mathrm{p}K_{\mathrm{BH}^+}$ values are known. As yet no complex of the series has been found which can be protonated

TABLE 17

Apparent $\mathrm{p}K_{\mathrm{BH}^+}{}^*$ and n values (eqn. (86)) for a series of isothiocyanato–metal complex indicators in aqueous sulphuric acid at 25.0°C

Complex ion	$\mathrm{p}K_{\mathrm{BH}^+}{}^*$	n
$[\mathrm{Co(NH_3)_5NCS}]^{2+}$	7.59	1.03
$[\mathrm{Rh(NH_3)_5NCS}]^{2+}$	7.26	1.07
cis-$[\mathrm{Co(en)_2NH_3(NCS)}]^{2+}$	7.50	1.10
trans-$[\mathrm{Co(en)_2NH_3(NCS)}]^{2+}$	7.61	1.12
trans-$[\mathrm{Co(en)_2H_2O(NCS)}]^{2+}$	8.15	1.03
$[\mathrm{Co(pn)_2NH_3(NCS)}]^{2+}$ (II)	7.82	0.92
cis-$[\mathrm{Co(en)_2(NCS)_2}]^{2+}$	6.27	1.31
trans-$[\mathrm{Co(en)_2(NCS)_2}]^{2+}$	8.56	1.38

in acidic solutions dilute enough for its pK_{BH^+} value to be determined directly. Thus there is no "anchor value" to which the others may be related by the stepwise comparison method.

The pK_{BH^+} values were determined as the H_0 value at which the complex is exactly fifty per cent protonated (i.e. $\log([BH^+]/[B]) = $ zero). The alternative method of extrapolation to infinite dilution was not preferred. The extrapolation involved is a large one and, as n is not exactly unity, could give rise to large errors in the value of pK_{BH^+} so determined.

All the transition metal complex indicators are positively charged so that the true acidity functions should be H_+ and H_{2+} as appropriate (see previous subsection). Thus all the $pK_{BH^+}{}^*$ values reported in Tables 17 and 18 are not the true thermodynamic pK values as they have been referred to H_0 (not H_+ or H_{2+} as appropriate). The asterisk[144] has been used to distinguish the quoted values from the true thermodynamic values. The difference between pK_{BH^+} and $pK_{BH^+}{}^*$ is probably a constant for a given charge type. Thus comparisons between the $pK_{BH^+}{}^*$ values are valid. If the n value is close to unity (eqn. (86)) then the use of slopes of plots of logarithm (rate constant) against $-H_0$ is valid. Many of the n values are close enough to unity for the complexes to be regarded as Hammett indicators.

Spectral changes have been observed when solutions of azido complexes of cobalt(III) are acidified[8, 145]. The rates of the subsequent hydrolysis reactions are too rapid to allow indicator ratio measurements. However, such measurements have been possible for the ion $[Rh(NH_3)_5N_3]^{2+}$ because the hydrolysis is very slow at 25°C. The measurements (Table 18) confirm that the $pK_{BH^+}{}^*$ value is different in different acids[145]. (This had already been suggested by kinetic measurements[8] – see Table 1.) The variation of $pK_{BH^+}{}^*$ from acid to acid has been attributed to ion-pairing. The substrates and their conjugate acids are all highly charged so strictly speaking we should rewrite the equation as $H_{2+} = -pK_{BH^{3+}} - \log([BH^{3+} \cdots\cdots X^-]/[B^{2+} \cdots\cdots X^-])$. Thus an extra factor is involved, i.e. ion-pairing. Hence the apparent $pK_{BH^+}{}^*$ value varies from acid to acid because of the different ion-pairing abilities of the anions concerned.

TABLE 18

Variation of $pK_{BH^+}{}^*$ and n value (eqn. 86) with solvent acid for the protonation of $[Rh(NH_3)_5N_3]^{2+}$ ion at 25.0

Acid	$-pK_{BH^+}{}^*$	n	Ref.
$HClO_4$	2.28	1.00	10
$HClO_4$	2.55	1.08	9
HCl	(ca. 1.8 [a])	1.30	9
H_2SO_4	2.01	0.98	9

[a] As the slope n is so different from unity the $pK_{BH^+}{}^*$ value given may be regarded as only an approximate measure of the base strength of B.

G. EVIDENCE FOR THE EXISTENCE OF PROTONATED SPECIES

The mechanisms discussed above require the existence of protonated forms of the relevant substrates. The existence of such species should, wherever possible be corroborated by non-kinetic methods. The following evidence is gleaned from preparative, spectroscopic and magnetic studies.

(i) Acido–ammine and acido–aquo complexes

Ugo and Gillard[146] have shown that the compound previously designated as the acid nitrate, viz. *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3.HNO_3$, is in fact the conjugate acid *cis*-$[Co(NH_3)_4\cdot(NO_2)(HNO_2)](NO_3)_2$. The infrared spectrum of the so-called nitric acid adduct has a broad band at ca. 3300 cm^{-1} due to the O–H vibration; this band is absent from the parent substrate. The ammine vibrations are unchanged when the complex is protonated. The spectrum of the "adduct" also has a new broad band at ca. 1670 cm^{-1}, which is also present in the deuterated analogue *cis*-$[Co(ND_3)_4NO_2(HNO_2)](NO_3)_2$. The conjugate acid of azidopentamminecobalt(III) ion has been isolated[147] as the impure solid, viz. $[Co(NH_3)_5N_3](ClO_4)_2\cdot 0.89HClO_4$. The impurity is probably unprotonated starting material. The infrared spectrum of the protonated compound had a peak at ca. 2200 cm^{-1} (antisymmetrical N_3 stretching mode) compared with ca. 2050 cm^{-1} for unprotonated azido ligands. The symmetrical N_3 stretching mode, ca. 1200–1400 cm^{-1} in the unprotonated form, was missing from the conjugate acid but may have been masked by the perchlorate bands.

Schmidt and Taube[148] have measured the proton affinity of the complex $[Co(NH_3)_5\cdot PO_4]$ in aqueous solutions. The acid dissociation of this compound is relatively slow, allowing accurate pH titrations to be performed. Titrations corresponding to the reactions

$$Co(NH_3)_5PO_4H^+ \rightleftharpoons Co(NH_3)_5PO_4 + H^+ \tag{87}$$

$$Co(NH_3)_5PO_4H_2{}^{2+} \rightleftharpoons Co(NH_3)_5PO_4H^+ + H^+ \tag{88}$$

(both at ionic strength 1.0 sodium perchlorate) were possible and the pK values do determined are 8.50 and 3.60 respectively. In 11.6 M perchloric acid or 18 M sulphuric acid a further spectral change occurs which Schmidt and Taube ascribed to the triprotonated species. Thus they were able to evaluate $K_3 = 4.7$, where

$$K_3 = \frac{[Co(NH_3)_5PO_4H_2{}^{2+}][H^+]}{[Co(NH_3)_5PO_4H_3{}^{3+}]} \tag{89}$$

for ionic strength 3.00 $NaClO_4$.

If the equilibrium K_3 is regarded as of the Hammett indicator type, and the concentrations of B and BH^+ are correlated with the Hammett acidity function for $HClO_4$–$NaClO_4$ ($I = 3.00$) mixtures[149], another estimate of K_3 may be made ($K_3 \sim 24.5$) (ref. 150). The agreement between the two different procedures is quite good. Nevertheless care should be taken when comparing data derived from the two different methods, i.e. the classical and the Hammett approaches. The discrepancy between the two sets of results will become greater as the acid concentration increases. This arises from the different assumptions, concerning activity coefficients, made in the two approaches.

The successive protonation constants of a series of phosphato complexes have been measured by Lincoln and Stranks[151,152]. In solutions of pH $\leqslant 1$ a titrimetric method was used whereas a spectrophotometric procedure was preferred for more concentrated perchloric acid solutions ($[H^+] = 1.0–11.0\,M$). The pK_a values of the complexes are collected in Table 19.

(ii) Cyano complexes

Schilt[153] has studied the protonation behaviour of a series of cyano complexes, viz. $[M(AA)_2(CN)_2]$ and $[M(AA)(CN)_4]^{2-}$ (where AA = 1,10-phenanthroline or 2,2′-dipyridyl and M = Fe, Ru, Os). The results showed that one proton could be added for each cyano group present. The infrared spectra showed that protonation of the metal atom, i.e. the formation of an M—H bond, did not occur[154]. Protonation probably takes place on the nitrogen atom of the cyano group. Experiments have been reported[155] in which the transition metal complex base and an organic base compete for an acid, e.g. $HClO_4$, in acetic acid as solvent, i.e.

$$B(HClO_4) + X \rightleftharpoons X(HClO_4) + B \tag{90}$$

where B = thiourea or *o*-chloroaniline and X = transition metal cyano complex. The so-called exchange constants were evaluated[158] and the results showed that for compounds of the type $[M(dipy)_2(CN)_2]$ the basicity is in the order Fe:Ru:Os = 1:3:14.

The acidity constants of the ions $Fe(CN)_6{}^{4-}$ and $Fe(dipy)(CN)_4{}^{2-}$, in aqueous solutions, have been evaluated[156]. The results show that the former is 300 times stronger a base than the latter. The acidity constants of ferro- and ferricyanide ions, in aqueous solu-

TABLE 19

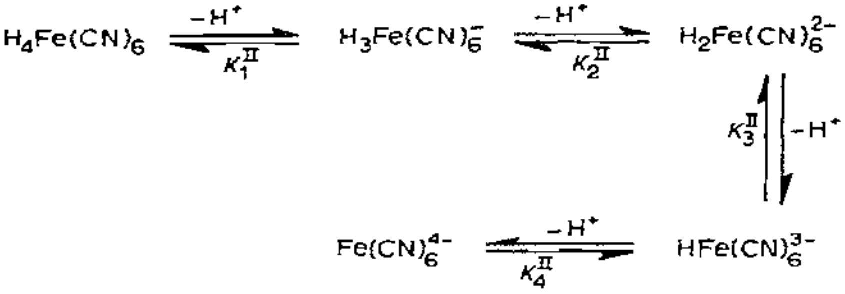
pKa_n values for the protonated forms of phosphato complexes (*n* denotes the number of protons on the acid form)

Complex	Temp	pK_{a1}	pK_{a2}	pK_{a3}
$(en)_2Co(OH_2)PO_4$	5.0	9.75	3.30	
	23.0	9.40	3.10	
	30.0	9.25	3.05	
$Co(NH_3)_4(H_2O)PO_4$	5	9.2	3.2	−0.34
$Co(en)_2PO_4$	5	4.25		
$Co(NH_3)_5PO_4$		8.50	3.60	−0.67 ($I = 3.0$)
H_3PO_4	19.7	12.5	5.92	+ 1.72
				−0.23 ($I = 0$)

tions, have been determined by pH titration. For the equilibria defined by scheme 29 the results showed

$$K_1^{\mathrm{II}} > K_2^{\mathrm{II}} > 0.1; K_3^{\mathrm{II}} = (6 \pm 2) \times 10^{-3}; K_4^{\mathrm{II}} = (6.7 \pm 0.3) \times 10^5$$

(the superscript refers to the oxidation state of iron and the subscript to the number of protons lost from the most highly protonated form, e.g. $H_4Fe(CN)_6$).



Scheme 29.

The results mean that at pH ~ 1, the concentration of $Fe(CN)_6^{4-}$ ion is negligible, the species $H_2Fe(CN)_6^{2-}$ predominating. Whenever pH > 1, the ferricyanic acid is completely dissociated.

The complex $[Fe(o\text{-phen})_2(CN)_2]$ forms a diprotonated species when dissolved in anhydrous hydrogen fluoride and a solid hexafluorophosphate salt was isolated[157]. Nuclear magnetic resonance studies showed that the compound had the *cis* configuration. Protonation probably occurs on the nitrogen atoms of the cyano groups.

(iii) 2,2′-Dipyridyl and 1,10-phenanthroline complexes

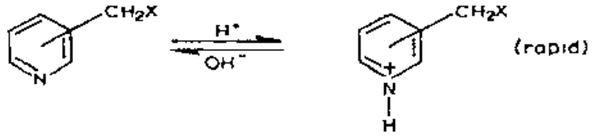
There is controversy concerning the existence, or otherwise, of protonated forms of the ions $[M(AA)_3]^{2+}$ (where M = Fe, Ru, Os; AA = 2,2′-dipyridyl or 1,10-phenanthroline).

Schilt[158] states that when the trisdipyridyl complexes of iron(II), ruthenium(II) and osmium(II) are acidified at temperatures below 0°C, no colour changes occur. Furthermore such solutions are stable for several hours. Schilt found that only acids which were also oxidising agents caused spectral or magnetic changes at ordinary temperatures. He concluded that these complexes have no measurable proton affinity. The variation of the redox potentials with acid concentration was also measured[160]. These results conflict with an earlier report in which Healy and Murmann[159] claim the existence of such protonated forms. These workers claimed that the protonations were accompanied by changes in the visible absorption spectra and paramagnetic moments (e.g. for $Fe(o\text{-phen})_3^{2+}$, μ_{eff} changed from 0 to 4.9 B.M.). It is noteworthy that they claimed that the spectral changes were *slow*.

This is in marked contrast to the behaviour expected for a rapid reversible protonation. Healy and Murmann ruled out a redox process because the colour changes could be reproduced in the presence of reducing agents (Sn^{2+} or $As(OH)_4{}^-$ ions).

(iv) Sigma-bonded organic ligands

An elegant study of an extensive series of pyridylmethyl—metal compounds has been reported[161], i.e.



(91)

(where CH_2X may be in the *ortho, meta* or *para* positions and X = (π-C_5H_5)$Fe(CO)_2$, (π-C_5H_5)$W(CO)_3$, (π-C_5H_5)$Mo(CO)_3$, $Mn(CO)_5$, $Co(CN)_5{}^{3-}$, HgCl and $Cr(H_2O)_5{}^{2+}$). The conjugate acids were prepared.

The strengths of the conjugate acids have been determined spectrophotometrically and the pK_a values have been used to assign approximate Hammett σ values to the organo-transition residue X. The "metallic group" substituents (X) appear to be amongst the strongest electron donating groups known. The pyridinium ions substituted in the 3-position are stronger than the 4-substituted analogues. Even so they are all very much weaker acids than the unsubstituted pyridinium ion, with the exception of the ions containing HgCl which causes an effect little different from that of the methyl group. The effects of the substituents are due to a combination of inductive and hyperconjugative electron donation. The protonation of *n*-cyanopyridinepentammineruthenium(II) ions, in which the ligand is coordinated via the cyano group, has been studied quantitatively[162]. The pK_a values of the protonated forms have been evaluated (Table 20) spectrophotometrically and compared with the pK_a values for the free ligands.

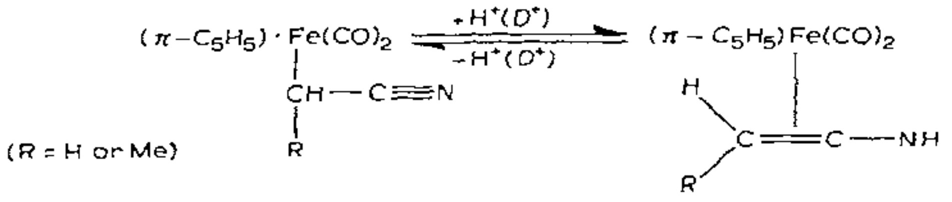
The conjugate acids were prepared by adding trifluoroacetic acid and then sodium perchlorate to a solution of the substrate complex. Coordination of the cyano-pyridine ligand causes a marked shift in ν_{CN} and protonation shifts it further still. Complexes containing ligands σ-bonded, via a carbon atom, to a metal may be protonated causing a marked

TABLE 20

pK_a values for the protonated forms of [Ru $(NH_3)_5$(*n*-CN–py)] ions

Isomer	pK_a complex	Free ligand	ΔpK_a
4-Cyano	2.72	1.90	0.82
3-Cyano	1.75	1.36	0.39
2-Cyano	0.80	−0.26	1.06

change in the bonding. 1-Cyanoalkyl–iron complexes are protonated by acids to form ketenimine compounds[163].

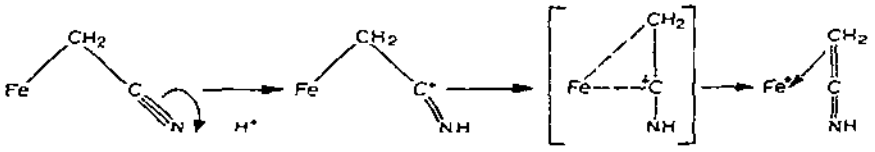


XX XXI

(92)

Yellow, crystalline XX is soluble in water and the protonated deep yellow form is very soluble. Salts of XX are relatively stable and may be handled in air for short periods. They were isolated as hexachloroantimonates and the infrared and nuclear magnetic resonance spectra studied. The infrared spectra showed the following: (*a*) the carbonyl stretching frequency was altered ~ 50 cm^{-1} on protonation – this is consistent with oxidation of the central metal ion; (*b*) the protonated (deuteronated) forms showed absorptions 3100–3400 cm^{-1} (N–H stretch), 2600–2400 cm^{-1} (N–D stretch), 1660 and 1470 cm^{-1} (N–H bend) and 1270 and 1145 cm^{-1} (N–D bend); (*c*) the unprotonated form absorbed at 2200 cm^{-1} (C≡N stretch) but this feature was absent from the spectrum of the protonated form.

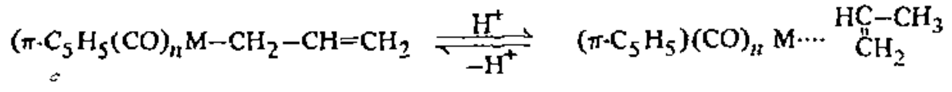
A mechanism for the protonation has been suggested (cf. metal–σ-allyl systems)



Scheme 30.

If this mechanism is correct the 2-cyanoethyl analogue should not undergo protonation. This is borne out by experiment.

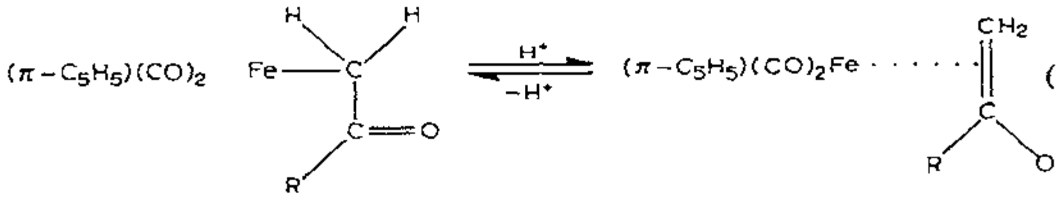
The protonated compounds are very interesting because they contain the ketenimine forms of acetonitrile and propionitrile stabilised by complex formation. Similarly σ-allyl compounds are protonated by acids, the product being a π-ethylenic complex, e.g.



$$(\pi\text{-}C_5H_5(CO)_n\underset{\sigma}{M}\text{–}CH_2\text{–}CH\text{=}CH_2 \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} (\pi\text{-}C_5H_5)(CO)_n\,M\cdots \begin{matrix} HC\text{–}CH_3 \\ \| \\ CH_2 \end{matrix} \qquad (93)$$

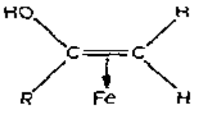
where M = Fe (*n* = 2) (ref. 165), Mo (*n* = 3) (ref. 166).

Oxoalkyl complexes are readily and reversibly protonated[164] forming cationic species which stabilise, by coordination, the enol forms of the organic ligand.

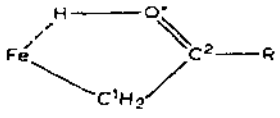


(94)

The most likely structures are XXII and XXIII.



XXII



XXIII

Scheme 31.

A distinction between XXII and XXIII is not possible using the available physical evidence, which is inconclusive. The absence from the ^1H NMR spectrum of a band assignable to *cis–trans* coupling of C^1 hydrogen atoms with C^2 hydrogen atoms favours XVIII. There are, however, no infrared bands assignable to the C–H stretches which should arise from the methylene structure. There is only one band in the region 2900–3200 cm^{-1} assignable to C–H as found for some (π-C_5H_5)iron olefin complexes. The distribution of positive charge to the metal is easier to interpret in terms of XXII.

(v) Pi-bonded systems

There are many examples of protonation of transition metal complexes which have considerable degrees of π-bonding. When the properties of such compounds are discussed, care should be taken to distinguish between the various possible protonation sites, e.g. protonation on the metal atom, on a ligand atom or on a π-electron cloud system.

The first example[168] of direct protonation of the central metal atom of a neutral complex was that of hydrido bis-π-cyclopentadienylrhenium(III), i.e.

$$(\pi\text{-}C_5H_5)_2ReH \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} (\pi\text{-}C_5H_5)_2ReH_2^+ \tag{95}$$

The cation may be precipitated with large anions; addition of base to the solution regenerates the neutral complex in quantitative yield. There are now many other examples, e.g.

$[HMo(\pi\text{-}C_5H_5)(CO)_3]^+$; $[HFe(CO)_3(PPh_3)_2]^+$

and some interesting binuclear species

$[\pi\text{-}C_5H_5M(CO)_3]_2H^+$ (M = W, Mo)

$[\pi\text{-}C_5H_5MoW(CO)_6]H^+$

$[\pi\text{-}C_5H_5M(CO)_2]_2H^+$ (M = Fe, Ru)

and

$[\pi\text{-}C_5H_5FeMn(CO)_7]H^+$ (refs. 167, 170)

These complexes are stable in, for example, concentrated oxygen-free sulphuric acid but only a few have been isolated as salts. The protonations are rapid and reversible in all cases except one (see below). Protonation on the metal atom was proved by infrared and nuclear magnetic resonance studies. The protonated species all displayed infrared absorption bands assignable to metal—hydrogen vibrations. The infrared spectra also showed that bridging carbonyl groups were absent from the binuclear species even though they were present in the unprotonated precursors, e.g. the pair $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2H]^+$.

The nuclear magnetic resonance spectra of the binuclear species all displayed metal—hydrogen resonances in the high field region (τ = 28.5—28.1). This resonance was not observed for the deuteronated analogues, e.g. $[\pi\text{-}C_5H_5FeMn(CO)_7]D^+$. Protonation of the cyclopentadienyl ring may be ruled out (for the protons of $\pi\text{-}C_5H_5$, $\tau \sim 4.5$). In the binuclear species the exchange between the hydrogen bound to metal and solvent protons is very slow. However, the NMR studies show that the hydrogen is associated with both metal atoms and undergoes rapid intramolecular exchange.

The compound $\pi\text{-}C_5H_5Fe(CO)_2\text{—}Mn(CO)_5$ dissolves in concentrated sulphuric acid but, in contrast to the other protonated species, the original base is not liberated on dilution with water. Solid salts of the protonated form have been isolated. The NMR spectrum of $[\{\pi\text{-}C_5H_5Fe(CO)_2Mn(CO)_5\}H]PF_6$ in liquid sulphur dioxide, unchanged at −70°C, is consistent with the proton being attached to the $\pi\text{-}C_5H_5Fe(CO)_2$ residue. This is a very interesting compound and appears to warrant further study.

It is interesting to note, however, that some other complexes which have metal—metal bonds, e.g. $Co_2(CO)_8$, $[Ph_3PCo(CO)_3]_2$, $[\pi\text{-}C_5H_5NiCO]_2$, $[\pi\text{-}C_5H_5Ni]_2RC{\equiv}CR$, $Ph_3PAuCo(CO)_4$ and $[\pi\text{-}C_5H_5W(CO)_3]_2Hg$, are decomposed by strong acids. It is apparent, therefore, that protonation behaviour of the type described above is not solely dependent on the presence of a metal—metal bond.

Chromium forms a series of complexes which enables the effect of ring substituent on basicity to be examined. Chromium carbonyl arene compounds $Cr(CO)_3Ar$ are protonated in BF_3, $H_2O\text{—}CF_3COOH$ solvent to yield yellow protonated species. All these arene complexes are weak bases. The effect of substituents in the phenyl ring, on the relative base strengths is such that base strengths follow the order: (ArH)mesitylene > toluene ~ 1,2-diphenylethane > *ortho*- and *para*-fluoro- or -chlorotoluene ≫ benzene > fluoro- or chloro-benzene. Solubility follows the same order. Sulphuric acid, however, rapidly decomposes these arene compounds. Similarly, some other protonated species, e.g. $Fe(CO)_5H^+$, are more stable in BF_3, H_2O-CF_3COOH than in concentrated sulphuric acid.

The complexes $(XPh_3)Fe(CO)_4$ and $(XPh_3)_2Fe(CO)_3$ (where X = P or As), dissolve in 98% sulphuric acid to yield yellow solutions containing protonated species. The stibine analogues are, however, decomposed within one minute.

Ferrocene, ruthenocene and osmocene are all weak bases, ferrocene being the strongest and osmocene the weakest. Ferrocene is protonated by propionic anhydride–boron trifluoride hydrate to yield ferrocinium cation. The NMR spectra show absorptions at unusually high field characteristic of metal–hydrogen bonding. There is no multiplet arising from the cyclopentadienyl ring protons, thus protonation of the C_5H_5 ring system is ruled out. Osmocene is a very weak base[171], rapid exchange between Os–H and solvent protons occurs in acidic solutions.

Molecular orbital calculations[172] confirmed the view that in hydridobis π-cyclopentadienyl metals, the metal to ring axes must be non-collinear and there are three spatially directed hybrid orbitals which may be occupied by hydrogen atoms or lone pairs of electrons. Thus complexes of the types $(\pi\text{-}C_5H_5)_2ReH$ or $(\pi\text{-}C_5H_5)_2WH_2$ should be readily protonated. This is borne out by experiment[168, 169]. Wilkinson and coworkers have postulated that the feeble basicity of ferrocene probably arises from the fact that the non-bonding (or partially bonding) orbitals only become spatially directed when the metal–ring axes are distorted from collinearity by molecular vibrations.

Hydrido complexes of osmium(II) may be made by the protonation of the osmium(0) complex $[(CO)_3(PPh_3)_2Os]$. The products are $[(CO)_3(PPh_3)_2OsH]X$ (where X = HCl_2, Br, ClO_4, BF_4 or PF_6) and behave as 1:1 electrolytes in nitrobenzene and are deprotonated by bases. The infrared spectra in the carbonyl absorption region suggest that the phosphine ligands are *trans* to each other and the hydrogen is in a plane with the three carbonyl ligands.

There are many reports of protonation and/or hydride formation in organometallic chemistry which, although related to the system described above, will not be discussed here. The systems listed at the end of this paragraph are considered to be outside the scope of this review for a variety of reasons. In one way or another they do not show simple acid–base behaviour in aqueous systems. Examples of departure from such simple behaviour are:

(1) Protonations are not rapidly reversible

(2) The protonated species are highly covalent hydride compounds of a higher oxidation state of the metal

(3) The protonated species are very unstable in aqueous solutions

(4) The protonated species once formed do not readily furnish protons in solution.

Such species are – WH_6L_3 (ref. 173), ReH_5L_3 (ref. 174), OsH_4L_3 (ref. 175), and IrH_3L_3 (ref. 176), (where L = PR_3), $HNi\{P(OC_2H_5)_3\}_4^+X^-$ (ref. 177), $[\{(C_6H_5)_2\text{-}PCH_2CH_2P(C_6H_5)_2\}_2NiH]X$ (where X = $AlCl_4$, BF_4 or HCl_2) (ref. 178), and

$[\{(C_6H_{11})_3P\}_2NiHCl]$ (ref. 179).

The protonation of polynuclear carbonyl complexes[181] may be associated with unusually high kinetic isotope effects[180]. Thus if $FeCo(CO)_{12}$ anion is protonated in aqueous solution using a mixture of concentrated hydrogen and deuterium chlorides, the rate of protonation by H_3O^+ was approximately seventeen times greater than that by D_3O^+. Such a kinetic isotope effect is considerably greater than expected for O–H and O–D bond cleavage in the transition state. The value for the isotope effect might be a function of the particular protonation site on the metal cluster, and so Mays and Simpson attempted to study various cluster compounds in various acids in the hope of gaining structural information. The investigation was hampered by (*a*) the lack of related cluster compounds which may be protonated and (*b*) many protonated species exchange protons with the protonating acid. In spite of these difficulties a few comparative results have been obtained (Table 21). The results show that variation of metal has little effect on the on k.

Another series, viz. $HRu_3(CO)_{12}{}^+$, $HOs_3(CO)_{12}{}^+$ and $H_2Ir(CO)_{12}{}^{2+}$ was studied[180]. The isotope effect (k) for the protonation of $Os_3(CO)_{12}$ is 11 ± 2. In the other cases, however, the rate of exchange with solvent is too fast to allow meaningful measurements.

TABLE 21

Kinetic isotope effects k_{H^+}/k_{D^+} (=k) for protonation of anionic carbonyl complexes

Complex	k
$FeCo_3(CO)_{12}{}^-$	16.8 ± 1.0
$RuCo_3(CO)_{12}{}^-$	15.4 ± 1.0
$OsCo_3(CO)_{12}{}^-$	16.2 ± 1.0

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