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To My Wife, Debbie

THE UNIVERSITY OF ALBERTA

HYDROLYSIS AND ELECTRON TRANSFER REACTIONS OF COORDINATED CYANOPHENOLS

by

© GEOFFREY BRIAN WRIGHT

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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OF

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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"HYDROLYSIS AND ELECTRON TRANSFER REACTIONS"
OF COORDINATED CYANOPHENOLS"

submitted by GEOFFREY BRIAN WRIGHT in partial fulfilment of the requirements for the degree of Master of Science.

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Supervisor

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Date 14th June 1972

ABSTRACT

The alkaline hydrolysis reactions of 3-cyanophenol and 4-cyanophenol complexes of pentaamminecobalt(III) have been studied. The rate of reaction was found to be first order with respect to hydroxide ion and the products of the reaction were the respective carboxamido complexes. The rate of hydrolysis of the benzonitrile ligand coordinated to the pentaamminecobalt(III) moiety was found to be greatly enhanced compared to the rate of hydrolysis of the free ligand. Changes in both the entropy and the enthalpy cause this effect. It was shown that the hydrolysis reaction was a facile method of preparation of N- bonded carboxamido complexes of pentaamminecobalt(III). A linear free energy relationship between the rate of hydrolysis of the substituted nitrile complexes and the Hammett σ substituent constant was observed.

The chromium(II) reduction of the 3-cyanophenol cobalt(III) complex was also studied. The rate of reduction was first order with respect to the chromium(II) concentration and independent of the hydrogen ion concentration. The product analysis data indicate that the reaction proceeds by two pathways: a major outer sphere path without ligand transfer and a minor inner sphere path with ligand transfer. In order to explain the sensitivity of the major path to substituents on the nitrile ligand a new mechanism consisting of an outer sphere electron transfer

with ligand reduction was proposed. The minor path was regarded as proceeding by inner sphere electron transfer with ligand reduction (radical ion or superexchange). For both of these mechanisms ligand reducibility is very important and good correlations between the rates of reduction of various substituted benzonitrile complexes and the reducibilities of the free ligands were obtained.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. Robert B. Jordan for his inestimateable help and guidance during this work.

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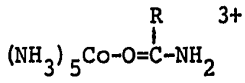
CHAPTER I

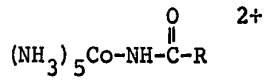
I N T R O D U C T I O N

Although the amino group of an amide is expected to be inherently more basic than the carbonyl oxygen [1] the available evidence [2] is overwhelmingly in favor of the oxygen being the most basic group. This is reflected many times in the fact that when an amide is coordinated to a transition metal ion the oxygen bonded isomer is normally obtained.[1] Both the N- and O-bonded formamide complexes of pentaamminecobalt(III) have been prepared [3], but the methods used previously do not seem widely applicable.

The preparation of the N-bonded carboxamide isomer presents an interesting problem in coordination chemistry as it provides a further example of linkage isomerism (1), (2). The N-bonded carboxamides are of interest because amido nitrogen coordination has been proposed [4] when a

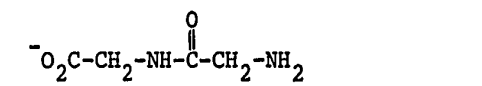


(1)



(2)

polypeptide such as glycylglycine (3) coordinates to transition metal ions.



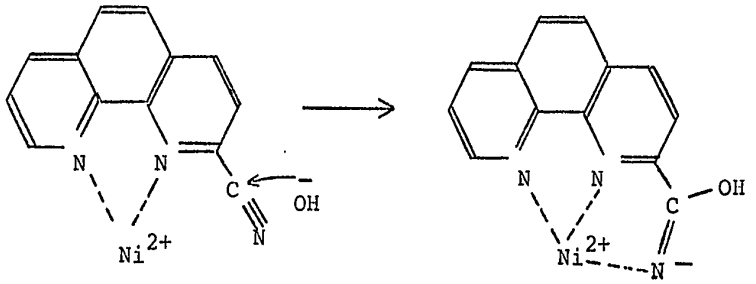
(3)

Studies of the simple carboxamide systems may provide guidelines as to the general coordination chemistry of the -NH-C(=O)- group.

It has been observed previously [5,6,7,8] that in the presence of transition metal ions the rate of hydrolysis of nitriles to the corresponding carboxamides is greatly enhanced. Normally the hydrolysis of nitriles requires vigorous reaction conditions.[9] From these rate studies of the hydrolysis of nitriles it is apparent that the ligands containing the nitrile groups interact with the transition metal ions in the transition state, followed by hydrolysis of the nitrile group. This facile hydrolysis of nitrile groups is an indication of the effect of the metal ion on the ligand. In this case the metal ion increases the susceptibility of the nitrile group to nucleophilic attack. Similar effects have been observed for the metal catalysed hydrolysis of the esters of amino acids.[10] Many other examples of changes of ligand reactivity upon coordination have been observed.[11]

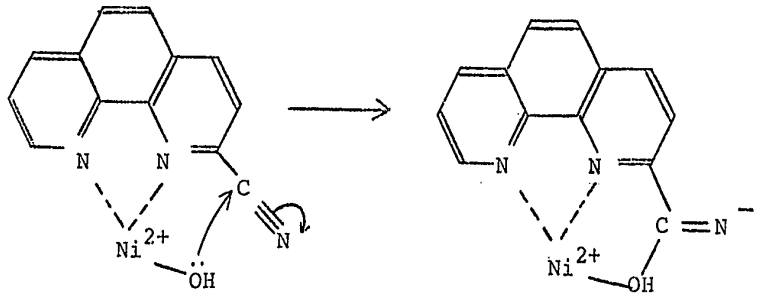
In the case of aromatic nitriles Breslow et al [5] have described the hydrolysis of 2-cyano-1,10-phenanthroline in the presence of nickel(II), copper(II) and zinc(II) ions. They propose that the 2-cyano-1,10-phenanthroline ligand coordinates to the nickel(II) ion through the two pyridine nitrogen atoms in the transition state. The hydration of

the free nitrile group is then extremely facile. These authors postulate two possible mechanisms for this reaction: attack of an external hydroxide on the complexed substrate (I-1), or attack of a coordinated hydroxide on the complexed substrate (I-2).



(I-1)

Carboxamide product



(I-2)

The authors provide evidence for mechanism (I-1) and propose that the rate enhancement of the hydrolysis of 2-cyano-1,10-phenanthroline by nickel(II) catalysis is due solely to the more positive entropy of activation found for this system. This indicates that the developing imino ion becomes bonded to the metal in the transition state. The fact that the activation enthalpies for the base catalysed and nickel(II) catalysed hydrolyses are very similar is probably due to the position of the nitrile group relative to the metal ion since any electronic redistribution on the ligand by the positive centre will not be very important for the remote nitrile group.

The alkaline hydrolysis reactions of nitrile bonded 3- and 4-cyanophenol complexes of pentaamminecobalt(III) have been investigated in this work as it is probable that the products of such reactions are the corresponding benzamido complexes bonded through the nitrogen atom. These reactions have been explored as they may provide a general method of the preparation of N-bonded carboxamides. In some previous work [3] the nitrogen and oxygen bonded isomers of formamide have been prepared by directly coordinating the ligand to the pentaamminecobalt(III) moiety. However, this method does not appear to be a general method of preparation of N-bonded amide complexes. The kinetic parameters of the hydrolysis reactions of the cyanophenol complexes were studied for comparison to those of the

nickel(II) catalysed hydrolysis of 2-cyano-1,10-phenanthroline and may provide evidence for mechanism (I-1) or (I-2). The substituted benzonitriles are particularly interesting ligands in this respect as the imino ion formed during the hydrolysis reaction of 2-cyano-1,10-phenanthroline would already be bonded to the cobalt(III) centre in this case. Therefore more positive activation entropies for the hydrolyses of the coordinated cyanophenols relative to the hydrolyses of the free ligands would agree with Breslow's [5] argument.

The chromium(II) reduction of the nitrile complexes was also of interest and the reasons are outlined in the following discussion of electron transfer reactions.

Electron transfer processes between transition metal ions in solution have been generally classified [12] into two major reaction pathways, one involving an inner sphere activated complex and the other an outer sphere activated complex. In the case of the outer sphere activated complex the electron transfer takes place between the reaction partners whilst their coordination spheres remain intact (I-1). When the electron transfer is mediated through a primary bond system, that is when a ligand is bonded to both the reductant and the oxidant in the activated complex, the mechanism is considered to be proceeding by an inner sphere mechanism (I-2).

$$Cr(OH_2)_6^{2+} + Co(NH_3)_6^{3+} + 6H^+ \rightarrow Cr(OH_2)_6^{3+} + Co^{2+} + 6NH_4^+ \qquad (I\text{-}1)$$

$$Cr(OH_2)_6^{2+} + Co(NH_3)_5X^{3+} + 5H^+ \rightarrow Cr(OH_2)_5X^{3+} + Co^{2+} + 5NH_4^+ \qquad (I\text{-}2)$$

Outer sphere reactions occur when the rates of substitution of the reacting metal ions are much slower than the rate of electron transfer. If one of the reaction partners, as in I-1, is substitution labile an outer sphere mechanism may still operate if the other partner does not have a suitable site for coordination to the labile metal ion. In I-1 the NH_3 group bonded to cobalt(III) does not have any unshared electrons to coordinate to the reductant, the chromium(II) ion. The theory of outer sphere electron transfer has stimulated much interest and various factors affecting the intimate details of this mechanism have been studied. The various points of view expressed have been summarised in a review by R. A. Marcus.[13]

Inner sphere reactions are most easily studied when one reaction partner is substitution inert and has a ligand capable of bonding to another more labile reaction partner. At least one of the products should also be substitution inert. Under these circumstances the ligand (X) can penetrate the coordination sphere of the labile species giving rise to the inner sphere activated complex (3):

$$[(NH_3)_5Co\text{-}X\text{-}Cr(OH)_2]^{5+} \qquad (3)$$

Clearly in order to observe inner sphere electron transfer reactions the reaction partners must be carefully selected. The cobalt(III)–chromium(II) electron transfer couple has been widely studied since cobalt(III) is relatively inert to substitution and chromium(II) is labile. Also the cobalt(II) and chromium(III) products of the electron transfer are labile and inert to substitution respectively. This is important because the bridging or mediating ligand is transferred to the chromium species during electron transfer and this chromium(III) complex will be generally stable and can be identified. In electron transfer reactions analysis of the products is important in determining the reaction pathway.

The intimate mechanisms of inner sphere electron transfer have been recently [14] classified into two general categories, the "chemical" and "resonance" mechanisms. The chemical mechanism refers to a process in which the reducing metal ion is strong enough to reduce the bridging ligand and the electron passes from a bound state on the reducing agent to a bound state on the ligand. In the "resonance" mechanism the electron is assumed to pass directly from a bound state on the reducing agent to

another on the oxidizing metal ion without occupying a bound state on the bridging ligand. Taube's [14] definition of the "resonance mechanism" includes the superexchange and direct exchange mechanism previously [15] proposed. The superexchange mechanism involves transfer of the electron from the reductant to the oxidant through a vacant ligand orbital, whereas the direct exchange mechanism indicates that the role of the bridging ligand is simply to bring the reactants together. Evidence supporting the superexchange mechanism [16], chemical mechanism [17,18] and the direct exchange mechanism [17] has been put forward in various systems.

Nordmeyer and Taube [17] proposed that a "chemical" or radical ion mechanism is operating for the reduction of the isonicotinamide ($4\text{-}NH_2C(O)C_5H_4N$) and the nicotinamide ($3\text{-}NH_2C(O)C_5H_4N$) complexes of pentaamminecobalt(III) by chromium(II). As the specific rate for reduction of the isonicotinamide complex is 500 times greater than for the nicotinamide complex the authors thought that the two isomers may be reduced by two different mechanisms. It was shown that the point of attack of the reductant was at the remote amide carbonyl oxygen in both complexes. This represents one of the few clear cases of remote group attack where the electron is passed through an extended conjugated system to the oxidant. One of the important factors affecting the rate of reduction of complexes by a

radical ion mechanism is the reducibility of the ligand; since the rate determining step for this reaction is the transfer of the electron from the reductant to the ligand. It has been found experimentally that free isonicotinamide is reduced at least 50 times faster than nicotinamide under the same conditions. Therefore if both the nicotinamide and the isonicotinamide complexes are being reduced by a radical ion mechanism the difference in the rates could be a reflection of the difference in the reducibilities of the ligands.

It has been proposed [3] recently that the reduction of the pentaamminecobalt(III) complexes of terephthalonitrile and 4-cyanophenol by chromium(II) proceeds by a radical ion mechanism. However, only in the case of the 4-cyanophenol complex has any ligand transfer been observed. As chromium(III) nitrile complexes have not yet been prepared it is possible that with terephthalonitrile the ligand transfer complex formed during reduction is very unstable and cannot be detected. The difference in the rates of reduction of the terephthalonitrile and 4-cyanophenol complexes ($0.92\ M^{-1}\ sec^{-1}$ and $2.96 \times 10^{-2}\ M^{-1}\ sec^{-1}$ respectively) for a radical ion mechanism can be explained in terms of the reducibility of the ligand as the free terephthalonitrile can be reduced polarographically whilst the 4-cyanophenol cannot.[19]

Another interesting system that is possibly proceeding by a radical ion mechanism is the reduction of the isomers of pentaamminecobalt(III) complexes of nitrobenzoic acid.[20] When chromium(II) is added to an acidic solution of p-nitrobenzoatopentaamminecobalt(III) the reductant is consumed rapidly but the cobalt(III) centre does not undergo any oxidation until more than 1 equivalent of chromium(II) has been added. This may indicate that the reducing electron has a significant lifetime on the ligand or that the NO_2 group is being reduced by the chromium. However, with the m-nitrobenzoatopentaamminecobalt(III) complex approximately 4 equivalents of chromium(II) are required before the cobalt(III) centre is reduced. It may be expected from simple conjugation arguments that the rate of electron transfer involving para substituents would be greater than when the substituents are in the meta positions. It is likely that the nitro group is first being reduced followed by reduction of the ligand and cobalt(III), but this does not explain the differences in the stoichiometric amounts of chromium(II) required for the para and meta isomers.

In order to study the effects of remote groups in electron transfer reactions the chromium(II) reduction of the 3-cyanophenol complex of pentaamminecobalt(III) has been studied. It should be noted that the nitrile systems have an advantage as far as a mechanistic study is concerned because there is no available site for adjacent

attack. Thus any mechanism for the reduction of this complex must be either outer sphere or involve the remote OH group. Also, a considerable amount of work [21] has been carried out on the reducibility of the nitrile ligands. Ligand reducibility is expected to be important for radical ion and superexchange mechanisms.

It was also shown [3] that in the reduction of the 4-cyanophenol cobalt(III) complex approximately 15% of the 4-cyanophenol was transferred to the reductant during electron transfer. The reduction was thought to be proceeding by two pathways; however, these paths could not be separated kinetically.

The work described here included a more extensive product analysis study than in the electron transfer of the 4-cyanophenol. This was expected to show more accurately the extent of ligand transfer. The OH function of the 3-cyanophenol complex is expected to be less acidic than in the 4-cyanophenol complex since in the meta position the OH group is out of conjugation with the electron withdrawing centre. If the formation of the bond between the reductant and the remote group is mechanistically important then a greater amount of ligand transfer is expected in the reduction of the 3-cyanophenol complex than obtained for the 4-cyanophenol complex.

CHAPTER II

E X P E R I M E N T A L

II (i) Preparation of Reagents

All reagent solutions were prepared with water redistilled from alkaline permanganate in an all glass apparatus. Lithium perchlorate solutions were prepared by dissolving reagent grade lithium perchlorate (G. F. Smith Chemical Co.) in water. The resultant solution was filtered through a 5 micron Millipore filter (Millipore Filter Corp.) and standardised by passing an aliquot through a column of Bio-Rad AG 50W-X8 cation exchange resin and determining the amount of hydrogen ion released. The sodium perchlorate solutions were prepared from reagent grade sodium perchlorate (G. F. Smith Chemical Co.) and standardised by the same method as the lithium perchlorate solutions. Perchloric acid solutions were prepared by dilution of 71.2% perchloric acid (J. T. Baker Chemical Co.) and standardised against sodium hydroxide. The standard sodium hydroxide solutions were prepared by dilution of ampoules of concentrated carbonate free reagent (Bio-Rad Laboratories).

Chromous perchlorate solutions were prepared by dissolving chromium metal (99.999% purity, United Mineral and Chemical Co.) in a dilute perchloric acid/lithium perchlorate solution under an atmosphere of high purity

argon (Union Carbide Ltd.). The total chromium content of these solutions was determined spectrophotometrically by oxidising an aliquot of the chromous perchlorate solution to chromate, with an excess of 30% hydrogen peroxide in potassium hydroxide solution. The absorbance at 372 nm was measured and the chromium concentration calculated from the known extinction coefficient of the chromate at this wavelength. The chromium(II) content of the chromous perchlorate solutions was determined periodically by reacting an aliquot of these solutions with an excess of standardised ferric ammonium sulphate solution. The excess ferric ion was determined by addition of potassium iodide and titration with a standard sodium thiosulphate solution. Sodium thiosulphate solutions were prepared by dilution of ampoules of concentrated reagent (Bio-Rad Laboratories).

Solutions for chromium(II) reductions were deoxygenated by purging with high purity argon and the reagents added by standard syringe techniques.

All other materials were used as supplied without further purifications.

II (ii) Preparation and Characterisation of Complexes

1. Carbonatopentaamminecobalt(III) nitrate $(NH_3)_5CoCO_3)(NO_3)$ and Aquopentaamminecobalt(III) perchlorate, $((NH_3)_5CoOH_2)(ClO_4)_3$

A solution of 450 g of ammonium carbonate in 450 ml of water and 700 ml of concentrated ammonium hydroxide was added to a solution of 300 g cobaltous nitrate in 150 ml of water and 50 ml of concentrated ammonium hydroxide. After stirring, the solution turned a deep crimson. This solution was air oxidised for 24 hours and a red solid gradually crystallised. The mixture was cooled in a refrigerator for 12 hours and the red crystals were filtered, washed thoroughly with methanol and ether, and finally air dried.

The carbonato complex was converted to aquopentaamminecobalt(III) perchlorate by slowly adding the red crystals to 500 ml of warm 1.0 M perchloric acid. This solution was heated, filtered and cooled. The aquopentaamminecobalt(III) perchlorate which crystallised out, was filtered and recrystallised from 1.0 M perchloric acid to remove all traces of nitrate. The product was washed with methanol and ether and air dried.

The aquopentaamminecobalt(III) perchlorate was characterised by carbon, hydrogen and nitrogen microanalysis and by its pmr spectrum in deuterated dimethyl sulphoxide. All the tau values quoted in Table 1 are relative to the solvent peak at τ 7.48. It has been observed that geometrically different ammine groups in pentaamminecobalt(III) complexes have different chemical shifts.[22,23] The assignment of the cis and trans ammine

TABLE 1

Proton Magnetic Resonance Data for Pentaamminecobalt(III) Complexes in Deuterated Dimethylsulphoxide [a]

Complex	trans NH_3	cis NH_3	Others
$((NH_3)_5CoOH_2)(ClO_4)_3$	7.19	6.22	OH_2 4.34
$((NH_3)_5CoNCC_6H_4OH)(ClO_4)_3$ [b,c]	6.59	6.14	C_6H_4 2.42, 2.53, 2.63, 2.80
$((NH_3)_5CoNCC_6H_4OH)(ClO_4)_3$ [d]	6.59	6.17	C_6H_4 2.09, 2.24, 2.87, 2.87, 3.01 OH 0.54
$((NH_3)_5CoNCC_6H_5)(ClO_4)_3$ [e]	6.47	6.06	C_6H_5 1.94, 2.05, 2.18, 2.21
$((NH_3)_5CoNHCOC_6H_5)(ClO_4)_2$ [e]	6.77	6.63	C_6H_5 2.20, 2.53

(a) All τ values are relative to the solvent peak at τ 7.48

(b) The OH peak could not be detected

(c) This is the 3-cyanophenol complex

(d) This is the 4-cyanophenol complex

(e) Reference 24.

protons is in accordance with integrated intensities and with previous work.[24]

Anal. Calcd for $((NH_3)_5CoOH_2)(ClO_4)_3$: N, 15.2; H, 3.69. Found: N, 15.25; H, 3.76.

2. 3-Cyanophenol Complex, $((NH_3)_5CoNCC_6H_4OH)(ClO_4)_3$

Aquopentaamminecobalt(III) perchlorate (5 g) was dissolved in 50 ml of trimethylphosphate with 15 g of Linde 3A molecular sieves. Then 5 g of 3-cyanophenol was added and this mixture was heated on a steam bath at approximately 70-80°C for 50 minutes. The initially red solution turned yellow-brown at the end of the reaction. This solution was filtered, cooled and added to 800 ml of secondary butyl alcohol. The mixture was stirred for 15 minutes and the product that was precipitated was collected by filtration. The precipitate was recrystallised by dissolving it in a minimum amount of warm water, adding a saturated solution of sodium perchlorate and cooling. The recrystallised product was collected by filtration, washed with ethanol, methanol and ether, and finally air dried. The product was further purified by ion exchange chromatography on Rexyn 102(H) (Fisher Scientific Co.) weak acid cation exchange resin in the sodium ion form. The complex was charged onto the ion exchange column and eluted with sodium chloride solutions of increasing concentrations from 0.1 M to 0.8 M. Using

this procedure a yellow band separated and moved down the ion exchange column leaving a red band which remained stationary. At this point the ion exchange column was cut and the yellow band was separated from the rest of the column. The yellow resin was thoroughly washed with water and methanol, and then air dried. A warm 2 M perchloric acid solution was stirred with the resin and most of the complex dissolved into the perchloric acid solution. The resin was removed from the mixture by filtration, and the purified complex was precipitated by addition of an equal volume of a saturated solution of sodium perchlorate and cooling.

The 3-cyanophenol complex was characterised by microanalysis and visible, ultraviolet, infrared and proton magnetic resonance spectroscopy. The pmr spectrum indicates a nitrogen bonded ligand according to an empirical rule proposed recently.[3] The rule states that the chemical shift difference between the cis and trans NH_3 protons is τ 1.0 - 1.5 for an O-bonded ligand coordinated to pentaamminecobalt(III) and τ 0 - 0.6 for an N-bonded ligand. A more theoretical discussion of the chemical shifts of cis and trans NH_3 protons in pentaamminecobalt(III) complexes has been given by Hendrickson and Jolly.[25]

The infrared spectrum of the 3-cyanophenol complex shows the typical absorptions of a coordinated NH_3 group

at frequencies 3200, 1625, 1330 and 860 cm^{-1}. Hexaamminecobalt(III) complexes show similar bands in these regions.[26] The C≡N stretching frequency of the nitrile complex is given in Table 2 together with that of the free ligand. The coordinated C≡N stretching frequency is somewhat increased relative to that of free 3-cyanophenol. This is also found to be the case for many pentaammineruthenium(III) nitrile complexes[27] and some rhodium(III) nitrile complexes.[28,29,30] Walton[31] indicates two factors that seem important in explaining this increase in stretching frequency. Simple calculations[32] show that coupling of the C≡N and M-N stretching vibration should give rise to a small increase in the C≡N stretching frequency, although the force constants remain the same as in the uncoordinated ligand. Also a small increase in the polar nature of the C≡N bond, as would be caused by coordination to a strongly positive centre, may give a shorter bond with a resultant increase in its stretching frequency. Purcell and Drago[33] calculated that the force constant of C≡N bond increased on coordination and more recently Purcell[34] stated that all nitriles coordinated to Lewis acids show this increasing force constant owing to a strengthening of the σ bonding between carbon and nitrogen. The increase of 40 cm^{-1} for ν(CN) upon coordination of a 3-cyanophenol to pentaamminecobalt(III) is typical of transition metal nitrile complexes.

TABLE 2

C≡N Stretching Frequencies for Nitrile Complexes [a]

Ligand	C≡N Stretching frequencies, cm^{-1}	
	Coordinated ligand	Free Ligand
3-Cyanophenol	2280	2240
4-Cyanophenol	2270	2230
Benzonitrile [b]	2270	2230

(a) All infrared spectra were run in KBr discs.

(b) Reference 24.

The visible and ultraviolet absorption spectral data of the 3-cyanophenol complex are given in Table 3. The complex shows an absorption maximum at a slightly higher energy than the low energy absorption of hexaamminecobalt(III) (ν_{max} at 339 and 476 nm) indicating the difference of an ammonia and a nitrile group in the spectrochemical series. The absorption at 340-350 nm, which is normally observed for pentaamminecobalt(III) complexes, appears to be hidden underneath the extremely intense absorption of the ligand in the 3-cyanophenol complex.

Anal. Calcd for $((NH_3)_5CoNCC_6H_4OH)(ClO_4)_3$: C, 14.9; N, 14.9; H, 3.56. Found: C, 15.1; N, 15.1; H, 3.64.

3. 4-Cyanophenol Complex $((NH_3)_5CoNCC_6H_4OH)(ClO_4)_3$

The 4-cyanophenol complex[35] was prepared by dissolving 5 g of aquopentaamminecobalt(III) perchlorate in 50 ml of trimethyl phosphate with 15 g of Linde 3A molecular sieves and 5 g of 4-cyanophenol. This mixture was heated on a steam bath (70-80°C) for two hours. The initial red colour of the solution turned to a yellow brown at the end of the reaction. The procedure for isolation and purification of the product was the same as that described for the 3-cyanophenol complex.

The 4-cyanophenol complex was charaterised by microanalysis and visible, ultraviolet, infrared and pmr

TABLE 3

Electronic Spectra of Pentaamminecobalt(III) Complexes [a]

Ligand	Absorption Maximum, nm (Extinction Coefficient M^{-1} cm^{-1})	
4-Cyanophenol	473(108)	295 (2.3×10^4)
3-Cyanophenol	469(80)	299 (2.8×10^3) 245 [b]
$4\text{-}NHCOC_6H_4O^{2-}$ [c]	493(114)	276 (2.0×10^4)
$3\text{-}NHCOC_6H_4O^{2-}$ [c]	487(82)	306 (3.1×10^3)
Benzonitrile [d]	469(79)	330(82) 233(2.2×10^4) [e]
$NHCOC_6H_5^-$ [d]	485(88.3)	345(117) 235(1.57×10^4)

(a) All spectra are in aqueous solution unless otherwise noted.

(b) Shoulder

(c) Obtained by dissolving the nitrile in 0.1 M NaOH

(d) Reference 24

(e) A shoulder is also observed at ~270 nm (2.6×10^3).

spectroscopy. The pmr results are shown in Table 1 and the chemical shift difference of the cis and trans NH_3 protons indicates nitrogen bonding of the 4-cyanophenol if the empirical rule previously discussed is applied.

The 4-cyanophenol complex shows the typical vibrations of coordinated NH_3 groups in its infrared spectrum. As shown in Table 2 the C≡N stretching frequency of the coordinated nitrile is increased by about 40 cm^{-1} relative to that in the uncoordinated nitrile. This is similar to the increase found for the 3-cyanophenol complex which was discussed previously.

The visible and ultraviolet absorption spectral data of the 4-cyanophenol complex are given in Table 3. The spectrum shows the same features as the 3-cyanophenol complex with the high energy d-d absorption hidden as before, although no absorption is observed at the 240 nm region.

Anal. Calcd for $((NH_3)_5CoNCC_6H_4OH)(ClO_4)_3$: C, 15.0; N, 15.0; H, 3.56. Found: C, 14.8; N, 15.0; H, 3.46.

II (iii) Kinetic Measurements

1. Alkaline Hydrolysis

The alkaline hydrolysis of the coordinated nitrile complexes was studied on an Aminco-Morrow stopped flow apparatus equipped with the standard high performance kinetic photometer, regulated D.C. power supply and a

standard storage oscilloscope. The temperatures of the reacting solutions in the drive syringes and in the spectrophotometer cell were maintained constant by pumping water from a Colora constant temperature bath through the block that surrounded the drive syringes and the cell. The temperature of the bath was regulated by a Fisher Thermistemp controller, with the thermistor probe in contact with the block containing the drive syringes and the cell. The temperature of the solutions in the drive syringes was measured periodically with a copper-constantan thermocouple. A refrigerator was placed into the temperature control system whenever necessary. In all alkaline hydrolysis experiments reacting solutions were allowed to stand in the drive syringes for fifteen minutes for temperature equilibration, before reaction.

The reaction was followed by the increase in absorbance with time at 420 nm for both the 3- and 4-cyanophenol complexes. A solution containing sodium hydroxide and sodium perchlorate at the required concentration was rapidly mixed with a solution containing the cobalt(III) nitrile complex and sodium perchlorate to give a final ionic strength of 1.0 M for the mixed solutions. The change in transmittance occurring during the reaction was displayed on the oscilloscope and a photographic record obtained. At each hydroxide ion concentration between 8 and 10 traces of the transmittance

change were obtained, and the rate constants reported are the average of these traces with a standard deviation of ~4%.

2. Chromium(II) Reduction

The reduction of 3-cyanophenolpentaamminecobalt(III) complex by chromium(II) was studied on a Bausch and Lomb Precision Spectrophotometer. The spectrophotometer was equipped with the standard water circulation system previously described. The temperature of the reaction cell and its contents was controlled by pumping water from the constant temperature bath through a specially made aluminum block which surrounded the reaction cell in the spectrophotometer. The thermistor probe was placed in contact with the aluminum block keeping the temperature of the reactant solution constant during the course of the reaction.

The reduction of the cobalt(III) nitrile complex was followed by the decrease in absorbance with time of the low energy (472 nm) cobalt(III) absorption. A reactant solution was prepared in a 5 cm reaction cell containing the nitrile complex, perchloric acid of required concentration, and lithium perchlorate to give a final ionic strength of 1.0 M. This solution was deoxygenated by passing pure argon through it for ten minutes, then the Cr^{2+} solution was added using the normal syringe procedures.

All the reduction reactions were run under pseudo-first-order conditions, with the Cr^{2+} concentration being at least 20 times greater than the nitrile complex concentration. The observed rate constant was determined from a plot of log $(A_t - A_\infty)$ vs time, where A_t is the absorbance at time t and A_∞ is the absorbance at infinite time.

The activation parameters of both the alkaline hydrolysis and the Cr^{2+} reduction reactions were determined using the transition state theory equation[36]:

$$\log \left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{2.303R}\left(\frac{1}{T}\right) + \left[\frac{\Delta S^{\ddagger}}{2.303R} + \log \left(\frac{\kappa k_B}{h}\right)\right]$$

where k is the specific rate constant in M^{-1} sec^{-1}, k_B is Boltzmann's constant, T is the temperature in °K, R is the gas constant in cal deg^{-1} $mole^{-1}$, $\Delta H^{\ddagger}$ is the enthalpy of activation and $\Delta S^{\ddagger}$ is the entropy of activation. A plot of log $\left(\frac{k}{T}\right)$ vs T^{-1} should be a straight line with slope $-\frac{\Delta H^{\ddagger}}{2.303R}$ and intercept $\left[\frac{\Delta S^{\ddagger}}{2.303R} + \log \left(\frac{\kappa k_B}{h}\right)\right]$. The transmission coefficient κ is assumed to be unity.

II (iv) Ion Exchange of the Reaction Mixtures

The products of all the reduction reactions were ion exchanged immediately after the reaction was completed. The contents of the reaction cell were charged onto a cationic ion exchange resin (Dowex 50W-X12), in the

hydrogen ion form, and separated at 5°C. The resin was then washed with 500 ml of water to remove all the free ligand from the resin. The charged reaction products were eluted with a solution 0.5 M in sodium perchlorate and 0.1 M in perchloric acid. This solution was added initially in a quarter strength and then the concentration was gradually increased to obtain separation.

It was discovered that the resin underwent a certain amount of decomposition in the air; the products of this decomposition appeared in the ultraviolet spectrum of the free ligand washed from the ion exchange column. Thus before each ion exchange experiment the resin was washed thoroughly with 2 M sodium hydroxide, distilled water, approximately 2 M perchloric acid, distilled water, ethanol, acetone and distilled water in that order. In this way any absorption in the ultraviolet spectrum from a source other than the reaction solution was removed.

II (v) Instrumentation

The proton magnetic resonance spectra were obtained using a Varian A56/60 spectrometer. The infrared spectra were obtained on a Perkin Elmer 421 grating spectrophotometer using potassium bromide discs and Nujol mulls as the media. All visible and ultraviolet spectra were recorded using a Cary Model 14 spectromphotometer.

CHAPTER III

RESULTS AND DISCUSSION

III (i) Alkaline Hydrolysis Reactions

The hydrolysis rates of the pentaamminecobalt(III) complexes of both 3-cyanophenol and 4-cyanophenol followed the rate law:

$$\frac{-d\ln[\text{complex}]}{dt} = k_{obsd} = k_1[OH^-]$$

The results of the kinetic study are given in Table 4 and plots of k_{obsd} *versus* hydroxide ion concentration at three different temperatures are shown in Figures 1 and 2. A typical kinetic plot is shown in Figure 3 and the data for this plot are given in Table 5. A summary of the kinetic results and the activation parameters is given in Table 6 along with the results from some other work[5,6,9,24], presented here for comparison.

Evidence will now be considered that indicates that the alkaline hydrolysis reaction of the nitrile coordinated complexes proceeds according to the following scheme (III-1):

$$(NH_3)_5CoN{\equiv}C\text{-}C_6H_4\text{-}X^{3+} + OH^- \longrightarrow (NH_3)_5CoNHC(=O)\text{-}C_6H_4\text{-}X^{2+} \qquad \text{(III-1)}$$

TABLE 4

Kinetic Results for the Hydrolysis of Pentaamminecobalt(III) Nitrile Complexes

Nitrile	Temp °C	$[OH^-]$ M	k_{obsd}, sec^{-1}	k_1 M^{-1} sec^{-1}
4-Cyanophenoxide	29	0.30	0.067	0.233
	29	0.40	0.097	0.243
	29	0.50	0.121	0.242
	34	0.20	0.076	0.380
	34	0.30	0.113	0.377
	34	0.40	0.159	0.398
	34	0.50	0.192	0.384
	40	0.20	0.125	0.625
	40	0.30	0.189	0.630
	40	0.40	0.267	0.668
	40	0.50	0.315	0.630
3-Cyanophenoxide	29	0.0125	0.030	4.80
	29	0.050	0.213	4.26
	29	0.075	0.380	5.07
	29	0.10	0.482	4.82
	29	0.20	0.996	4.98
	29	0.30	1.40	4.67
	35	0.075	0.52	6.93
	35	0.15	1.12	7.47
	35	0.30	2.20	7.33
	35	0.40	3.04	7.60
	40	0.075	0.919	12.3
	40	0.20	2.50	12.5
	40	0.30	3.62	12.1
	40	0.40	4.92	12.3

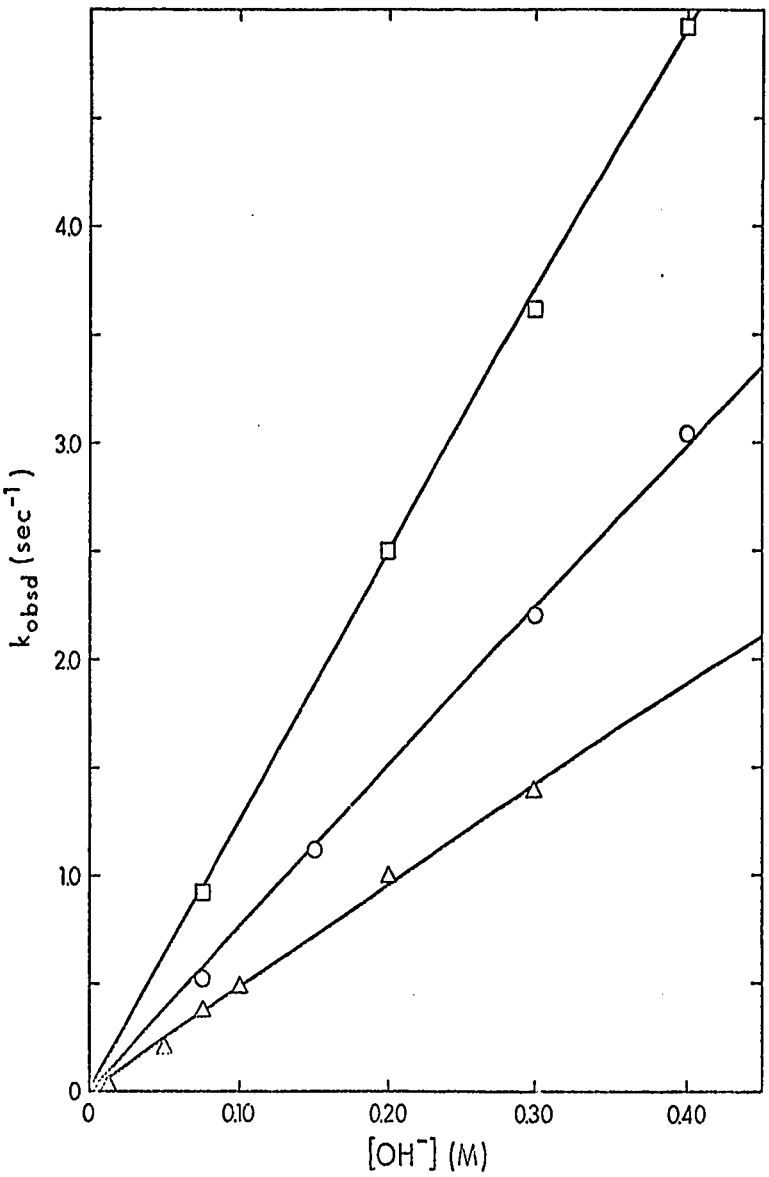


FIGURE 1. Dependence of the Hydrolysis Rate of the 3-Cyanophenolpentaamminecobalt(III) Complex on [OH^-], Ionic Strength 1.0 M ($NaClO_4$): Δ, 29.0°; O, 35.0°; □, 40.0°.

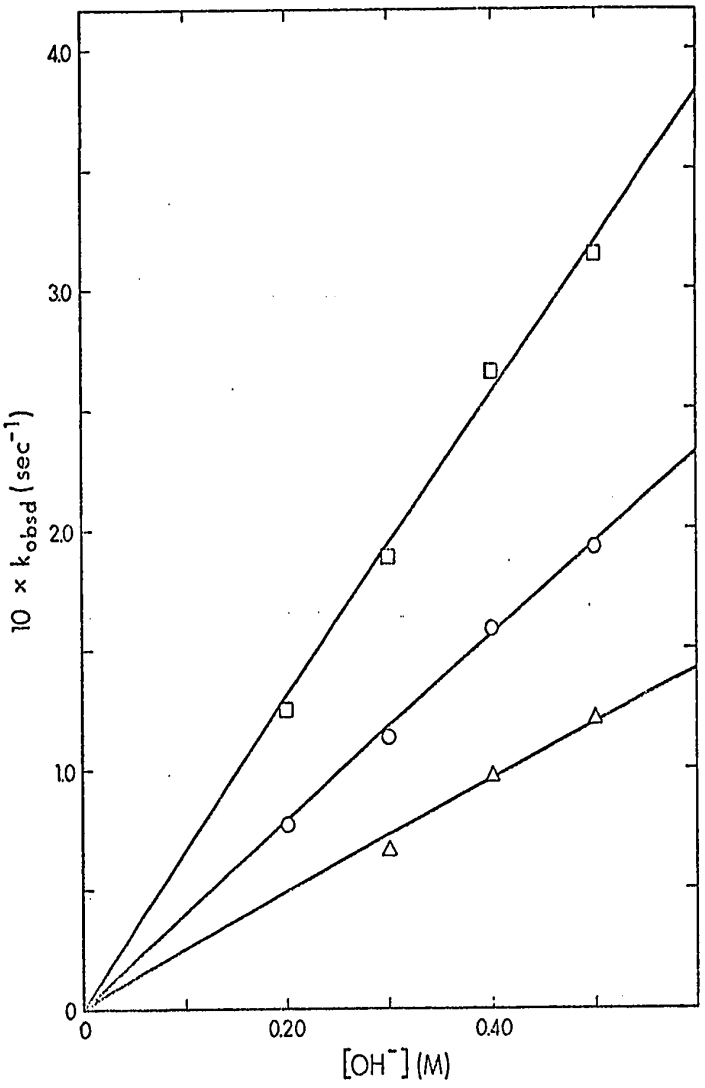


FIGURE 2. Dependence of the Hydrolysis Rate of the 4-Cyanophenolpentaamminecobalt(III) Complex on [OH^-], Ionic Strength 1.0 M ($NaClO_4$): Δ, 29.0°; O, 34.0°; □, 40.0°.

TABLE 5

Data for a Typical Kinetic Experiment [a]

Temperature	=	29°C
Hydroxide ion concentration	=	0.1 M
Ionic strength	=	1.0 M ($NaClO_4$)
Infinite transmittance	=	88.1%

Time (sec)	T_t % [b]	$\log \frac{T_\infty}{T_t}$ [c]
0	76.0	0.0642
0.5	78.4	0.0507
1.0	80.1	0.0414
1.5	81.4	0.0344
2.0	82.7	0.0275
2.5	83.8	0.0218
3.0	84.6	0.0176
3.5	85.1	0.0151
4.0	85.7	0.0120
4.5	86.2	0.0095
5.0	86.5	0.0080
5.5	86.8	0.0065

(a) The concentration for 3-cyanophenolpentaammine-cobalt(III) complex was ~1.0×10^{-3} M.

(b) T_t is the percentage transmittance at time t.

(c) T_∞ is the percentage transmittance at infinite time.

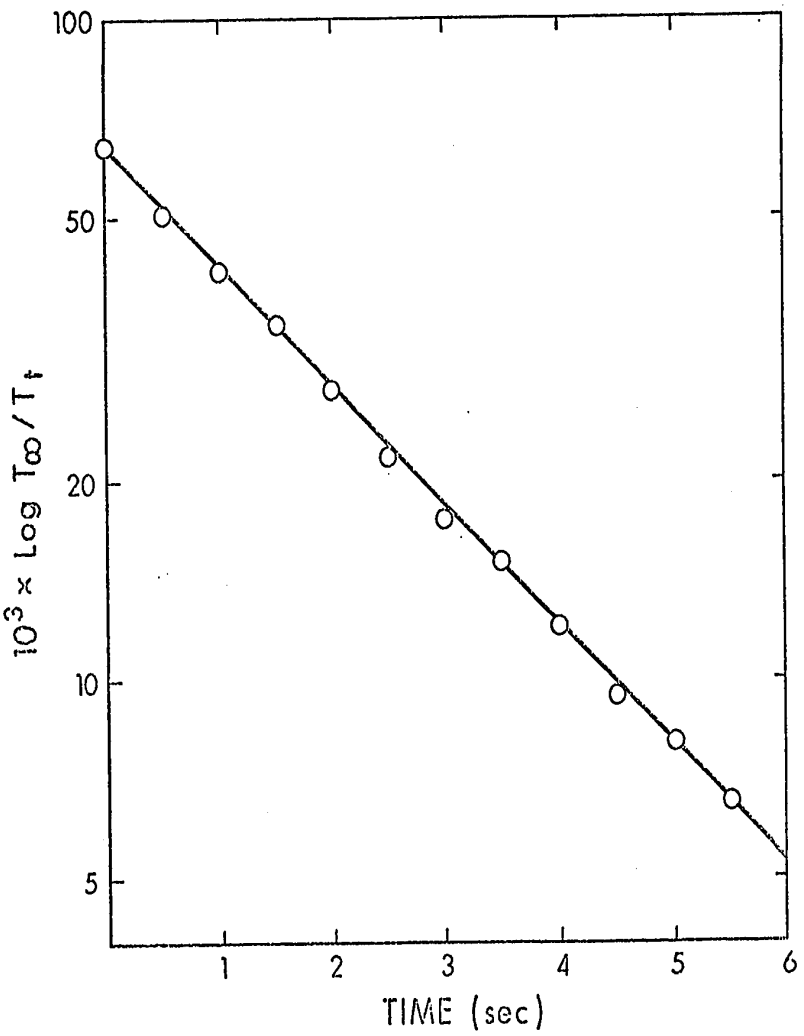


FIGURE 3. Typical Hydrolysis Kinetic Plot

TABLE 6

Summary of Kinetic Results for Alkaline Hydrolysis of Nitriles

Compound	Rate Constant M^{-1} sec^{-1} 25.6°	$\Delta H^{\ddagger}$ kcal $mole^{-1}$	$\Delta S^{\ddagger}$ cal $mole^{-1}$ deg^{-1}
$(NH_3)_5Co(4\text{-cyanophenoxide})^{2+}$ a	0.18	16.3 ± 1.5	-7.4 ± 4
$(NH_3)_5Co(3\text{-cyanophenoxide})^{2+}$ a	3.57	15.1 ± 1.5	-5.5 ± 4
$(NH_3)_5Co(benzonitrile)^{2+}$ b	18.8	16.5	2.7
Benzonitrile c	8.2×10^{-6}	19.9	-15.2
p-Chlorobenzonitrile c	7.2×10^{-6}	17.4	-19.3
Ni(2-cyano-1,10-phenanthroline)$^{2+}$ d	2.4×10^{4}	15.1	14
2-Cyano-1,10-phenanthroline d	2.6×10^{-3}	15.7	-20
Ni(2-cyanopyridine)$^{2+}$ e	6.3×10^{7}	13.7	23

(a) This work in $NaOH - NaClO_4$ at $\mu = 1.0$ M.

(b) Reference 24 also in $NaOH - NaClO_4$ at $\mu = 1.0$ M.

(c) Reference 9 in 50% aqueous acetone. In calculating the rate constants at 25.6°C it was found that Wiberg's results are better reproduced by the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ given here.

(d) Reference 5.

(e) Reference 6.

The product from the benzonitrile complex where X = H, has been isolated and the chemical analysis[24] and the pmr spectrum (given in Table 1) are as expected for a N-bonded benzamide complex. The infrared spectrum of the product shows that the C≡N stretching mode has been lost consistent with the formation of the carboxamide product and and an absorption at 1660 cm^{-1} can be assigned to the C=O stretch vibrations expected for this product.

Table 3 includes electronic spectral data for the hydrolysis products of the 3-cyanophenol, 4-cyanophenol and benzonitrile complexes together with the spectral data of the unreacted complexes. The similarity of the shifts in the electronic spectra on hydrolysis of the cyanophenol and benzonitrile systems indicates that the former also give rise to an N-bonded carboxamide as the hydrolysis product. The limited amount of nitrile complex prevented characterisation of the hydrolysis product in the cyanophenol systems.

The alkaline hydrolysis of the cyanophenol complexes of cobalt(III) appears to be an example of a general method of preparation of N-bonded substituted benzamide complexes. Normally preparations of amide complexes yield the oxygen coordinated isomer.[3] The chromium(II) reduction of the protonated and unprotonated forms of the N-bonded benzamide complexes may be of interest.

It is apparent from Table 6 that coordination to a

$(NH_3)_5Co^{3+}$ moiety increases the rate of benzonitrile hydrolysis by a factor of ~2 x 10^6. The difference in the activation enthalpy for the hydrolysis of the uncoordinated and coordinated benzonitrile is of the order of 3.5 kcal $mole^{-1}$ whereas the difference in the activation entropies of these two systems is 17 cal $mole^{-1}$ deg^{-1}. The latter factor contributes about 5 kcal $mole^{-1}$ at 25°C to the free energy of activation ($\Delta G^{\ddagger}$) calculated from:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

Thus both a more favourable $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are contributing significantly to the rate enhancement.

Clearly then any explanation of the increase of the rate of hydrolysis of benzonitrile upon coordination to a cobalt(III) centre by consideration of a single activation parameter cannot be justified since the activation parameters contribute almost equally to the free energy of activation for this reaction. However, it is interesting to note that a plot of the log of the specific rate constant at 25.6°C versus the activation entropy (Figure 4) does indicate a qualitative linear relationship. Only the hydrolysis of 2-cyano-1,10-phenanthroline and benzonitrile are exceptions to this relationship.

Table 6 also shows that the rate of alkaline hydrolysis of the 3-cyanophenol complex is approximately 20 times greater than that of the 4-cyanophenol complex.

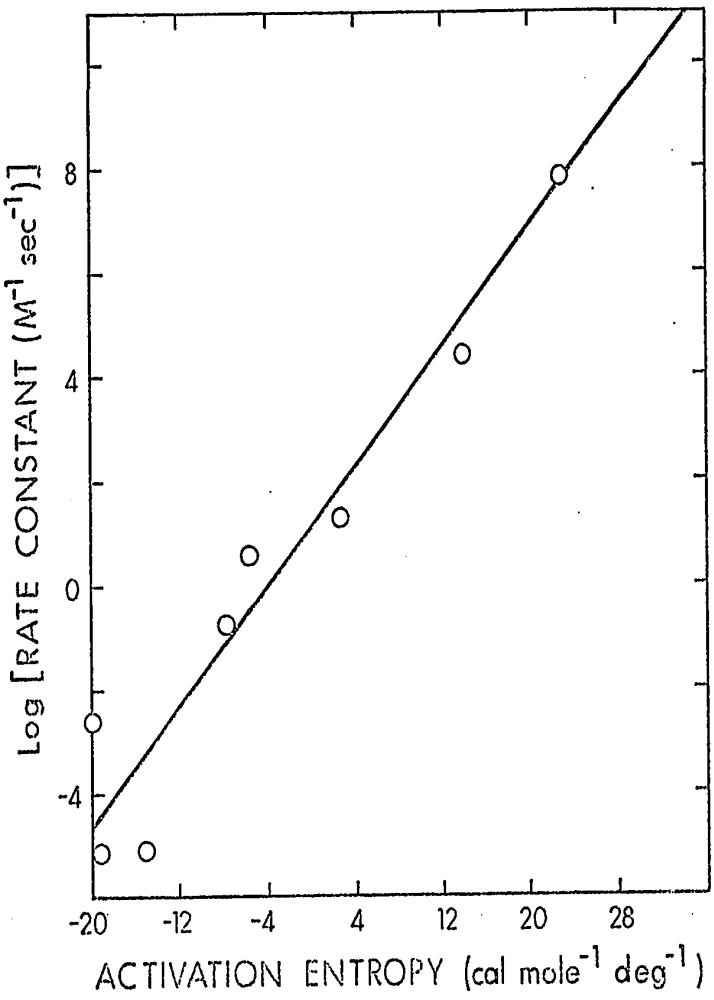


FIGURE 4. Relationship Between the Log of the Specific Rate Constant and the Activation Entropy for a Number of Systems.

This rate difference is probably a reflection of a change in the electronic distribution within the ligand brought about by the change in position of the $-O^-$ substituent. Simply the electron donating power of the $-O^-$ group to the reaction centre is somewhat reduced when it is in a meta position compared to an $-O^-$ group in a para position. Thus nucleophilic attack at the -CN group by hydroxide ion is expected to be faster for the meta substituted ligand.

It has been found previously [9,37] that the rate constants for hydrolysis of substituted benzonitriles show a linear free energy relationship. Wiberg plotted the rate of hydrolysis of a series of such nitriles with hydroxide and hydroperoxide ions versus the Hammett σ constants and found a linear relationship. He used the normal σ_p and σ_m constants for para and meta substituents. Cohen and Jones observed a similar relationship to exist between a different series of benzonitriles and the Hammett σ_p constants. A linear free energy relationship for the coordinated nitriles studied here was obtained. The appropriate data is given in Table 7 and plotted in Figure 5. The slope of the line in Figure 5 gives a reaction constant (ρ) of 3.84 for this particular reaction.

The rate enhancement of $\sim 2 \times 10^6$ for the alkaline hydrolysis of the coordinated cyanophenols relative to the uncoordinated benzonitrile is of a similar magnitude

TABLE 7

Linear Free Energy Relationship Data

Ligand	Substituent	log k	σ [a]
4-Cyanophenoxide	O^-	-0.7447	-0.52
3-Cyanophenoxide	O^-	0.5527	-0.19
Benzonitrile	H	1.2742	0.

(a) These σ values are the normal σ_p and σ_m constants, as obtained from reference 46.

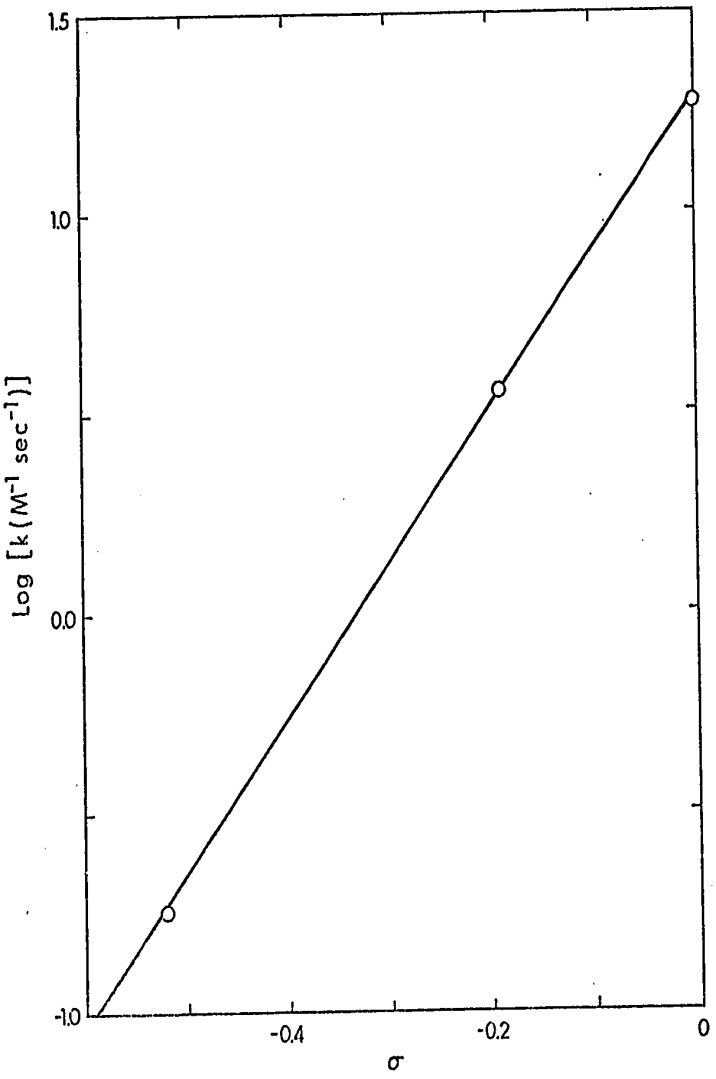


FIGURE 5. Relationship Between the Rates of Hydrolysis of the Cyanophenol Complexes and the Hammett σ Substituent Constants.

to the value of 10^7 observed by Breslow et al [5] for the 2-cyano-1,10-phenanthrolinenickel(II) system. It must be remembered, however, that the two cases are somewhat different in that the nitrile is not initially bound directly to the metal in the latter case while it is in the former system. Thus in the 2-cyano-1,10-phenanthrolinenickel(II) system the nitrile is initially remote from the effects of the central metal ion. It is also less sterically hindered than a nitrile coordinated to a $(NH_3)_5Co^{3+}$ moiety. The kinetic parameters for the catalysis differ in the cobalt(III) and nickel(II) cases. The $(NH_3)_5Co^{3+}$ system appears to give both a more favourable $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, while with the nickel(II) [5,6] complexes only $\Delta S^{\ddagger}$ is affected significantly. However, the change of $\Delta S^{\ddagger}$ to a more positive value for the hydrolysis of the coordinated nitriles is at least qualitatively consistent with the argument of Breslow et al [5] that the more favourable $\Delta S^{\ddagger}$ with the nickel(II) complex is associated with bonding of the developing imino ion to the metal in the transition state. In the system studied here the imino group is already bonded to cobalt(III).

III (ii) Chromium(II) reduction of 3-Cyanophenolpentaamminecobalt(III).

The chromium(II) reduction rate of the 3-cyanophenolcobalt(III) complex followed the rate law:

$$\frac{-d(\ln[\text{cobalt(III) complex}])}{dt} = k_{obsd} = k_1[Cr^{2+}]$$

The rate data for the reduction of this complex is given in Table 8 and plots of k_{obsd} versus chromium(II) concentration at 25°C, 35°C and 45°C are shown in Figure 6. A typical kinetic plot is shown in Figure 7 and the appropriate data for this plot is given in Table 9. The rate constants and the activation parameters are summarised in Table 10.

In general it has been found that kinetic parameters alone are not sufficient to establish the electron transfer mechanism. The identification of the initial products of the reduction reaction is the most important factor in determining the mechanism of the reaction and the point of attack of the reductant. The existence of a chromium(III) ligand complex, in this particular case, where the ligand was originally coordinated to the cobalt(III) centre is conclusive evidence for an inner sphere mechanism; however, the lack of such a complex, which shall be referred to as a ligand transfer complex, does not necessarily mean that an inner sphere mechanism is not operating. The latter

TABLE 8

Kinetic Results for the Reduction of the 3-Cyanophenolpentaamminecobalt(III) Complex [a]

Temp °C	$[Cr^{2+}] \times 10^{-2}$ M	$[H^+]$ M	$k_{obsd} \times 10^{-3}$ sec^{-1}	$k_1 \times 10^{-2}$ $M^{-1}\ sec^{-1}$
25	4.1	0.05	1.80	4.38
25	4.3	0.30	1.87	4.36
25	2.0	0.30	0.79	3.96
25	3.4	0.35	1.37	4.04
25	3.4	0.35	1.43	4.20
35	3.2	0.05	2.10	6.89
35	1.9	0.30	1.31	6.88
35	2.0	0.30	1.46	7.30
35	4.2	0.30	2.95	7.02
35	3.1	0.35	2.20	7.10
45	3.2	0.05	3.96	12.4
45	2.0	0.30	2.39	11.2
45	4.4	0.30	5.78	13.1
45	3.2	0.68	3.96	12.4

(a) The ionic strength was kept at 1.0 M with lithium perchlorate for all the kinetic experiments.

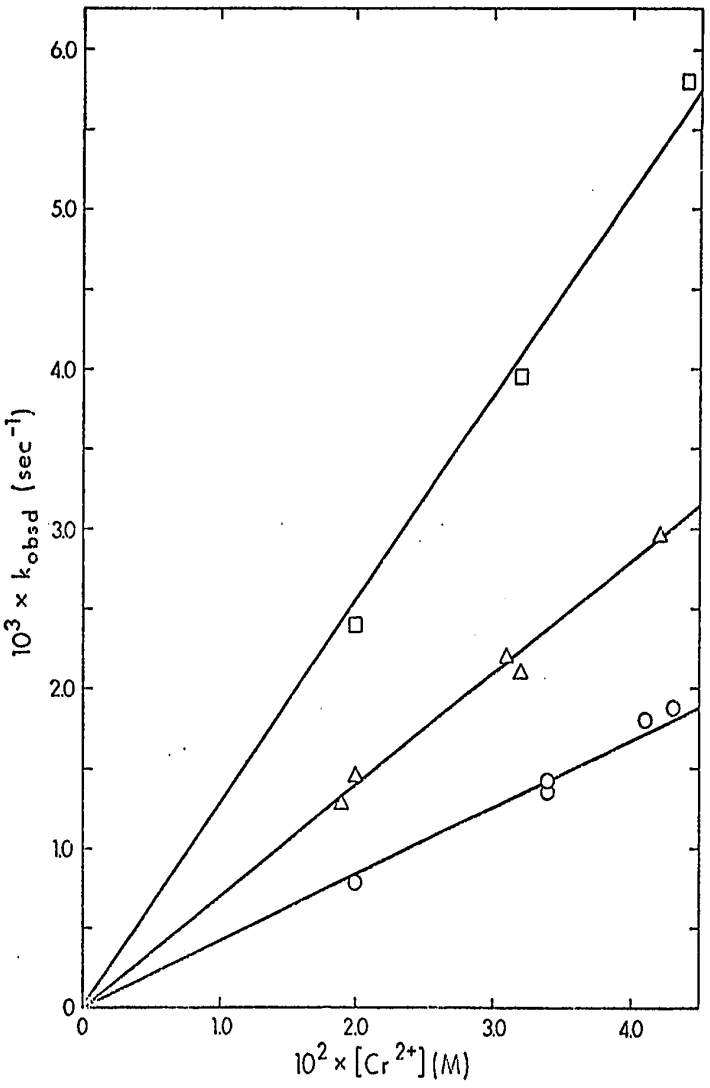


FIGURE 6. Dependence of the Reduction Rate of the 3-Cyanophenolpentaamminecobalt(III) Complex on $[Cr^{2+}]$, Ionic Strength 1.0 M ($LiClO_4$): O, 25.0°; Δ, 35.0°; □, 45.0°.

TABLE 9

Data for a Typical Reduction Kinetic Experiment

Temperature = 35°C

Chromium(II) concentration = 2.0×10^{-2} M

Ionic strength = 1.0 M $LiClO_4$

Hydrogen ion concentration = $3,0 \times 10^{-1}$ M

Infinite transmittance = 72.0%

T_t% [a]	$\log \frac{T_\infty}{T_t}$ [b]	Time (secs)
28.8	0.398	0
33.4	0.334	120
37.5	0.283	240
41.6	0.238	360
45.7	0.197	480
49.1	0.166	600
52.2	0.140	720
54.8	0.119	840
57.0	0.102	960
59.3	0.084	1080
61.3	0.070	1200
63.2	0.057	1320
64.6	0.047	1440
65.3	0.042	1560
66.4	0.035	1680
67.5	0.028	1800
67.8	0.026	1920
68.6	0.021	2040
69.2	0.017	2160
69.6	0.015	2280

(a) T_t is the percentage transmittance at time t.

(b) T_∞ is the percentage transmittance at infinite time.

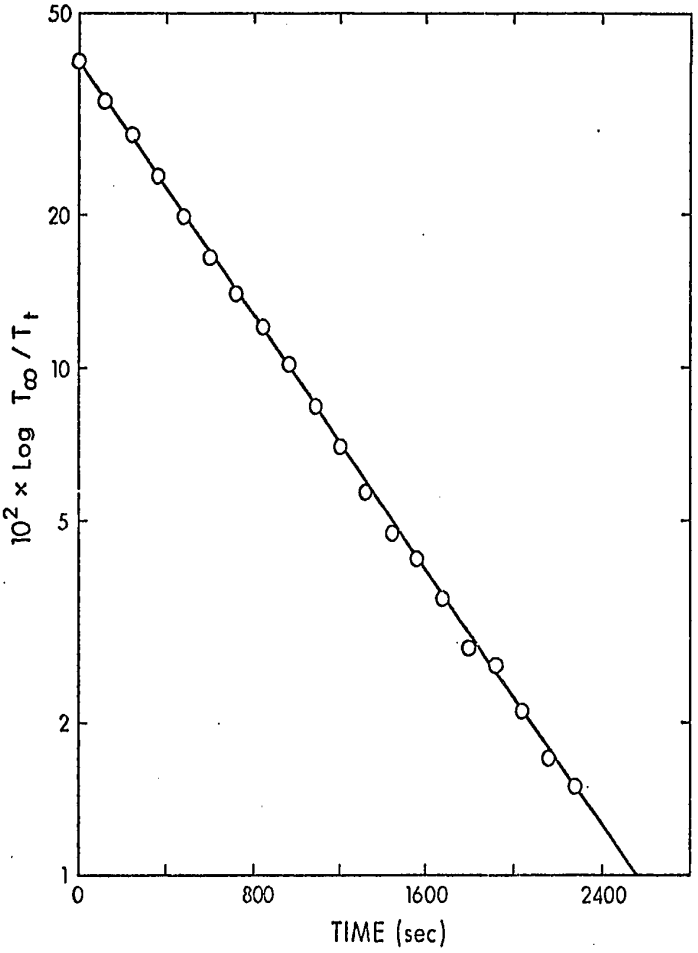


FIGURE 7. Typical Reduction Kinetic Plot.

TABLE 10

Kinetic Parameters for the Reaction of the 3-Cyanophenol-pentaamminecobalt(III) Complex

Ligand	Temp °C	k M^{-1} sec^{-1}	$\Delta H^{\ddagger}$ kcal $mole^{-1}$	$\Delta S^{\ddagger}$ cal $mole^{-1}$ deg^{-1}
3-Cyanophenol	25	4.17×10^{-2}	9.4 ± 1	-34 ± 3
	35	7.07×10^{-2}		
	45	1.23×10^{-1}		

possibility may be the case if the chromium(III) complex is undergoing a fast hydrolysis reaction to $Cr(H_2O)_6^{3+}$ before it can be characterised. However, pentaaquochromion(III) complexes are normally stable with respect to hydrolysis.[38]

Clearly the analysis of the products of the reaction of the 3-cyanophenol cobalt(III) complex forms a very important part of the study of the reduction of this complex. The percentage of ligand transfer can be obtained by directly determining the amount of the ligand transfer complex after reaction or by determining the amount of the uncoordinated ligand after reaction. Normally both of these methods are used together to act as a check. However, if only a small percentage of the reaction is going with ligand transfer, then the amount of ligand transfer product becomes difficult to detect. This is because it is very difficult to separate the ligand transfer complex from the relatively large amounts of $Cr(H_2O)_6^{3+}$ by ion-exchange chromatography and also the extinction coefficients of the complex in the visible and ultraviolet region are expected to be very small. In the 3-cyanophenol case the percentage of ligand transfer in the reaction was obtained by determining the percentage of the free ligand in the reaction products.

The solutions of the reaction products were air oxidised for five minutes and were subjected to cation

exchange chromatography as previously discussed in Chapter II. The free ligand passed through the cation exchange column and was collected for quantitative spectrophotometric analysis. The electronic spectrum of the uncoordinated ligand showed that no chemical change, such as reduction, had occurred to the ligand. The percentages of the uncoordinated 3-cyanophenol are tabulated in Table II. From a consideration of this data the free ligand recovered after reaction is independent of the hydrogen ion and the temperature. Therefore, the amount of reaction proceeding by a ligand transfer mechanism is also independent of these two parameters. The mean percentage of the 3-cyanophenol recovered is 88.0% with a standard deviation of 3.1%. The question may be raised as to whether the 12% of the ligand not recovered is the result of some experimental loss and as such does not reflect the amount of ligand transfer complex formed. The ligand transfer complex would be very difficult to detect as its concentration must be very small and also there would be a large excess of Cr^{3+} present in the air-oxidised reaction mixture. In fact no ligand transfer complex was detected. An experiment was performed, therefore, in which the products of the reaction were left for eight days at room temperature before being ion exchanged. The free 3-cyanophenol recovered from the experiment was 95.1%. The 5% discrepancy from 100% free ligand that one might expect to obtain

TABLE 11

3-Cyanophenol Recovered after the Reduction Reactions

Temp °C	$[Cr^{2+}] \times 10^{-2}$ M	$[H^+]$ M	$[Cr^{3+}] \times 10^{-3}$ M	Percentage 3-Cyanophenol %
25.0	4.1	0.05	1.14	88.1
25.0	4.0	0.68	1.07	91.5
35.0	3.0	0.05	1.25	88.2
35.3	3.0	0.05	1.23	88.9
35.0	3.2	0.30	1.26	88.4
35.0	4.1	0.30	1.08	90.5
35.0	1.9	0.30	1.10	90.0
35.0	4.3	0.30	1.07	86.2
35.0	4.3	0.30	1.19	82.3
35.0	2.0	0.30	1.17	80.4
35.0	2.0	0.30	1.20	95.1[a]
35.5	2.96	0.68	1.17	85.7
35.5	2.96	0.68	1.27	93.7
45.0	3.2	0.05	1.07	89.5
45.0	4.4	0.30	1.26	90.2
45.0	2.0	0.30	1.19	89.4
45.0	3.2	0.30	1.10	87.8
45.0	2.96	0.68	1.17	86.2
45.0	3.2	0.68	1.15	87.3

(a) In this particular case the reaction mixture was ion exchanged eight days after the reaction was completed.

could be due to a very slow rate of hydrolysis of the pentaaquochromium(III) complex. It has been shown [3] that the chromium(III) complex of 4-cyanophenol hydrolyses very slowly even at 45°C. The same author has shown that this complex in the presence of excess chromium(II), does undergo some slow hydrolysis. This apparent chromium(II) catalysed hydrolysis probably involves electron transfer to yield $Cr(H_2O)_6^{3+}$ and 4-cyanophenol pentaaquochromium (II). The latter complex is expected to be labile and will lose the cyanophenol ligand, as shown in (III-2) below, where X represents the 4-cyanophenol:

$$Cr(H_2O)_6^{2+} + Cr(H_2O)_5X^{3+} \xrightarrow{\text{slow}} Cr(H_2O)_6^{3+} + Cr(H_2O)_5X^{2+}$$

$$\text{fast} \quad \downarrow \quad H_2O$$

$$Cr(H_2O)_6^{2+} + X$$

(III-2)

Thus this scheme does give rise to a pathway producing the free ligand. In the experiment where the reduction products were left for eight days before ion exchange there was an excess of chromium(II) present and thus hydrolysis of the 3-cyanophenol chromium(III) complex by the above pathway would be expected yielding a recovery of 100% free phenol.

There is a further possibility that the 5% free ligand that was not recovered in the original experiment may be retained by the resin itself and not eluted. A further experiment was performed where a solution of the ligand of known concentration was passed through the column, collected and the concentration determined. All of the 3-cyanophenol ligand was recovered. Therefore no retention of the ligand by the resin occurred. Although it is not clear what the causes of the 5% discrepancy of the free ligand may be, it can be said with certainty that some ligand transfer is occurring, the amount being approximately 7%.

Any mechanism postulated for the reduction of the 3-cyanophenol complex of pentaamminecobalt(III) by chromium(II) must explain not only the observed kinetic results but also the results of the product analyses. A possible mechanism operating is one that involves two distinct pathways, a normal outer sphere reaction as the major pathway together with a much smaller inner sphere pathway. This mechanism as a possible explanation of the experimental data will now be considered, although the intimate mechanism of the inner sphere path will be discussed later when inner sphere mechanisms and ligand reducibilities are considered.

In a normal outer sphere mechanism the ligand coordinated to the cobalt(III) centre formally takes no part in

the detailed electron transfer mechanism. The transfer of the electron is directly from an orbital of the reductant into an orbital of the oxidant as shown in Scheme I-1. However, to say that the electron transfer is completely independent of the ligands in outer sphere reactions is not strictly true since it is thought that in some cases a large conjugated ligand, such as o-phenanthroline, can increase the delocalisation of the electron on the reductant and thereby make electron transfer to the oxidant more facile.[14]

The acetonitrile complex, $(NH_3)_5CoNCCH_3^{3+}$, has been studied [39] and the rate of reduction by chromium(II) found to be 0.017 M^{-1} sec^{-1}. This reaction must proceed via an outer sphere mechanism since there is no group on the oxidant with a pair of electrons available to form the bridged species with the reductant. A study of the chromium(II) reduction of the malonodinitrile complex of cobalt(III) [39] yields a rate constant which is at least 100 times greater than the acetonitrile complex. The malonodinitrile complex, $(NH_3)_5CoNCCH_2CN$, has a remote site available for coordination to the reductant. Insofar as the rate of reduction of the 3-cyanophenol (4.17×10^{-2} M^{-1} sec^{-1}) is close to the rate of reduction for an outer sphere mechanism, the 3-cyanophenol system may proceed by a major outer sphere pathway with a small ligand transfer path. However, the rate of reduction is not a very

dependable criterion for a particular mechanism, but is at best a guideline. Similarly activation parameters cannot be used as being definitive of a mechanism, but it has been observed [3] that as a general rule reduction of nitrile complexes with a less positive activation energy than ~11 kcal $mole^{-1}$ and a more negative entropy than ~-30 cal mol^{-1} deg^{-1} should not be considered as proceeding by a simple outer sphere path. The activation parameters for the reduction of the 3-cyanophenol complex are $\Delta H^{\ddagger}$ 9.4 kcal $mole^{-1}$ and $\Delta S^{\ddagger}$ -34 cal $mole^{-1}$ deg^{-1}.

Reactions proceeding by an outer sphere mechanism would be expected to have a rate of reduction that was independent of small changes in the ligands coordinated to the oxidant. These changes are such that they are not likely to change the ligand field strength of the particular ligand and thus have no effect on the energies of the cobalt(III) d-orbitals. This type of difference in ligands is exemplified by the 3- and 4-cyanophenols. However, the rate of reduction of these two nitrile complexes differs by about 30%, as shown in Table 12. While the difference in rate is not large it is still significant as far as the outer sphere mechanism is concerned. Two other examples with larger variations in their rates of reduction are the terephthalonitrile and nitrile bonded 4-cyanobenzoic complexes of pentaamminecobalt(III). The rates of re-

TABLE 12

Activation Parameters for the Chromium(II) Reduction of Some $(NH_3)_5CoX$ Complexes

Ligand	k(25°C) $M^{-1}sec^{-1}$	$\Delta H^{\ddagger}$ kcal $mole^{-1}$	$\Delta S^{\ddagger}$ e.u.
3-Cyanophenol	4.17×10^{-2}	9.4 ± 1.0	-34 ± 3
Terephthalonitrile [a]	0.920	5.5	-40
Isonicotinamide [b]	4×10^{-3}	9	-39
Fumarato [c]	1.32	6.7	-36
4-Cyanophenol [a]	3.0×10^{-2}	11.1	-28

(a) Reference 3

(b) Reference 17

(c) Reference 40, for the 2+ species.

duction are 0.92 M^{-1} sec^{-1} [3] and 0.282 M^{-1} sec^{-1} respectively. If all four of these complexes are being reduced by an outer sphere mechanism then their rates of reduction would not be expected to differ so widely.

One major alternative to a simple outer sphere pathway is an inner sphere mechanism involving ligand transfer. Three different intimate mechanisms have been suggested for inner sphere paths which would be consistent with the sensitivity of the rate of reduction to the nitrile ligand. The first is the radical ion mechanism whereby the reductant electron reduces the ligand (III-3), where X is the ligand.

$$(NH_3)_5CoX^{3+} + Cr(H_2O)_6^{2+} \longrightarrow (NH_3)_5Co^{III}\text{---}X\text{---}Cr^{II}(H_2O)_5$$

$$\downarrow \quad \text{slow}$$

$$(NH_3)_5Co^{III}\text{—}\dot{X}\text{—}Cr^{III}(H_2O)_5$$

$$\downarrow \quad \text{fast}$$

$$Co^{II} + XCr^{III}(H_2O)_5$$

(III-3)

Secondly a superexchange mechanism may be operating (III-4):

$$(NH_3)_5CoX^{3+} + Cr(H_2O)_6^{2+} \longrightarrow (NH_3)_5Co^{III}\text{---}X\text{---}Cr^{II}(H_2O)_5$$

$$\downarrow \text{ slow}$$

$$(NH_3)_5Co^{II}\text{---}X\text{---}Cr^{III}(H_2O)_5$$

$$\downarrow \text{ fast}$$

$$Co^{II} + XCr^{III}(H_2O)_5$$

(III-4)

The third possibility is the direct exchange mechanism where the ligand serves only to bring the oxidant and reductant together and its orbitals are not involved in the actual transfer of the electron.

However, all these three mechanisms give rise to a chromium(III) ligand transfer product and as such they can only be considered as viable possibilities if the chromium(III) complex undergoes fast hydrolysis. As previously discussed pentaaquochromium(III) complexes are usually stable to hydrolysis so this possibility is not very likely. Also R. J. Balahura [3] has shown that the rate of hydrolysis of the 4-cyanophenolpentaaquochromium(III) complex is very slow relative to the time required for reduction of the cobalt(III) complex and the ion exchange of the products of the reaction. Results of this study with the 3-cyanophenol complex indicate that it is

also slow to hydrolyse on the same time scale since only 88% free cyanophenol is recovered. Therefore, the major part of the reaction cannot occur by an inner sphere pathway. A discussion of which of the mechanisms might give rise to the small inner sphere path that is found to occur will be given later when the effect of the ligand reducibility is considered.

It can be seen clearly that neither a simple outer sphere nor a simple inner sphere mechanism can satisfactorily explain the experimental results obtained. The rate of reduction of the 3-cyanophenol complex and the associated activation parameters together with the large variation of the rate with small changes in the substituent on the aromatic ring of the ligand are not consistent with an outer sphere mechanism for the reduction reaction. However, an inner sphere mechanism is not consistent with the small amount of ligand transfer observed since the chromium(III) ligand transfer complex is expected to be stable. Therefore it is necessary to postulate an alternative detailed mechanism to those so far discussed.

This third mechanism involves an outer sphere reduction by a stepwise electron transfer from the reductant to the ligand with the formation of a radical ion, followed by the transfer of the electron by the ligand to the cobalt centre. This mechanism can be considered to be an outer sphere radical ion (III-5) or outer sphere

superexchange mechanism. The lifetime of the radical formed is the only difference in these two mechanisms. In the case of the radical ion mechanism the ligand radical has a definite lifetime whilst the superexchange mechanism implies that the reducing electron is simply transferred through a ligand orbital to the oxidant.

$$(NH_3)_5CoX^{3+} + Cr(H_2O)_6^{2+} \longrightarrow [(NH_3)_5Co^{III}X(H_2O)Cr^{II}(H_2O)_5]$$

$$\downarrow \text{ slow}$$

$$(NH_3)_5Co^{III}\dot{X} + Cr^{III}(H_2O)_6$$

$$\downarrow \text{ fast} \qquad \text{(III-5)}$$

$$Co^{II} + X + Cr^{III}(H_2O)_6$$

The radical ion mechanism has been proposed for the chromium(II) reduction of the fumarato [40] and the isonicotinamide [17] complexes. However, for these two systems the inner sphere reduction path has been conclusively proven by the isolation and identification of the chromium(III) ligand transfer complexes. These reactions are characterised by a low enthalpy of activation and a large negative entropy of activation. Table 12 shows the activation parameters of the reduction of the 3-cyanophenol complex together with the activation parameters of the reduction of other complexes, including the isonicotinamide and

fumarato complexes, for comparison. The activation parameters of the 3-cyanophenol reduction are quite similar to those of the isonicotinamide and fumarato complexes.

The reducibility of the ligand is thought to be an important factor in the radical ion and superexchange mechanisms of the reduction of the cobalt(III) centre.[41] The relative reducibilities of a series of related ligands can be obtained by a consideration of the polarographic half-wave potentials of the reduction of these ligands. Zuman [21] has shown that a linear free energy relationship can be obtained between the polarographic half-wave potential and the Hammett σ^- substituent constants for a series of substituted benzonitriles. The σ^- substituent constants were utilised by Zuman as they included an enhanced mesomeric effect by strong electron donating groups when they are in conjugation with the reaction centre. They were originally introduced by Hammett [42], when he proposed the use of a special σ^- constant for the nitro substituent for reactions of phenoxide ions and anilines. In this context it should be noted that there is no direct correlation with the normal Hammett σ constants. Table 13 shows the data for a linear free energy relationship plot between the log of the rate of reduction of some substituted benzonitrile ligands coordinated to pentaamminecobalt(III) and the Hammett σ^- constants of the substituents. This plot is shown in Figure 8. As the value of the σ^- constant

TABLE 13

Data for the Linear Free Energy Relationship of the Rate of Reduction of Some $(NH_3)_5CoX$ Complexes

Ligand	k(25°C) M^{-1} sec^{-1}	σ Constant
Terephthalonitrile	0.92[a]	0.91[b,c]
3-Cyanophenol	4.17×10^{-2}	0.12[d]
4-Cyanophenol	2.96×10^{-2} [a]	-0.11[b,e]
4-Cyanobenzoic acid	0.282[f]	0.73[b,d]
Benzonitrile	4.27×10^{-2} [g]	0

(a) Reference 3

(b) These values are modified Hammett σ constants called σ^-. The σ^- values are determined from the reactions of phenols or amines, and are used whenever the substituent has a strong mesomeric interaction with the reaction site.

(c) Reference 43

(d) Reference 44

(e) This value of the σ^- constant is the value given by Wells [43] for the $-OCH_3$ substituent, the σ^- for the -OH substituent being unavailable.

(f) The value of the rate constant quoted here was obtained from a preliminary study of this complex. Further work is in progress in this laboratory

(g) Reference 45

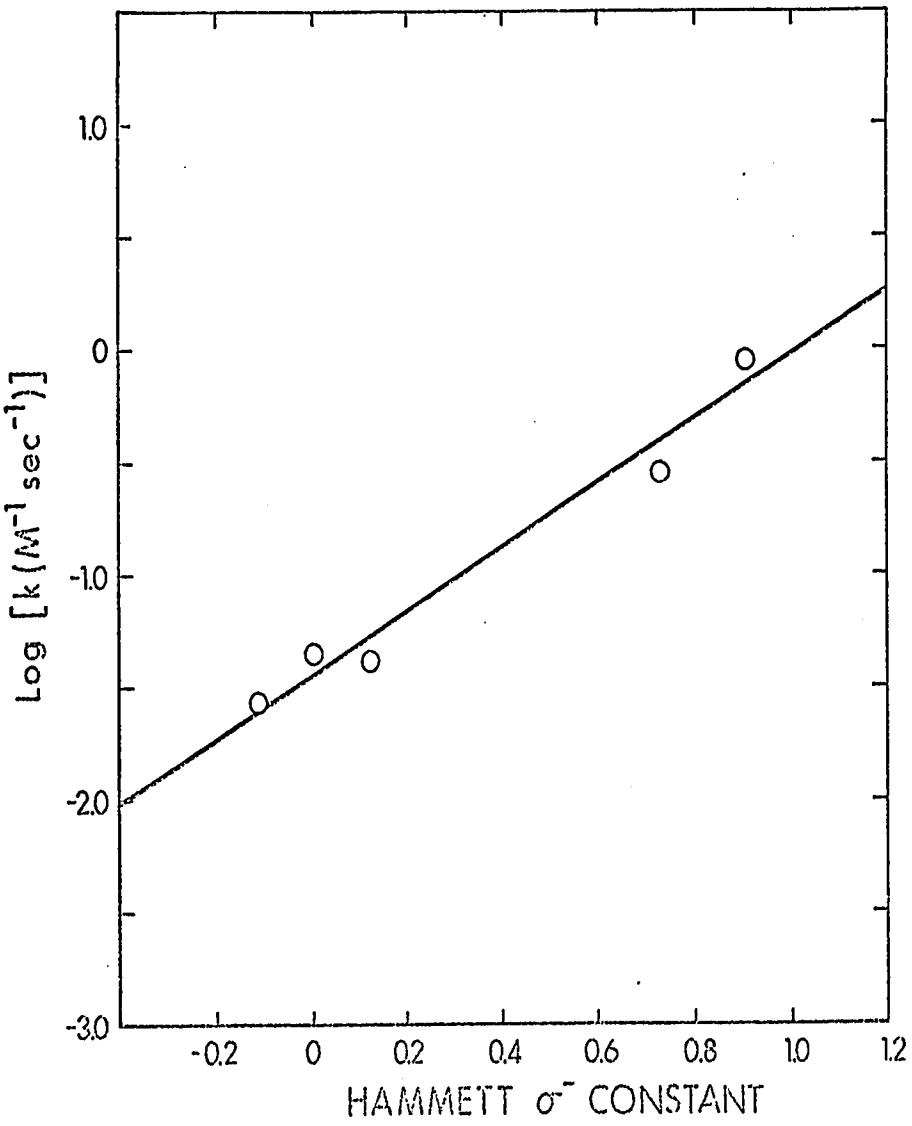


FIGURE 8. Relationship between the Rates of Reduction of Nitrile Complexes of Pentaamminecobalt(III) and the Hammett σ^- Substituent Constants.

for the para substituted OH group was not available a value for the para OCH_3 group was used instead. It might be expected that the substituent constants for the OH and OCH_3 groups would be very similar. A difference may arise owing to the fact that a methyl group is more electron donating than a hydrogen atom. However, this slight difference in electronic effects should only manifest itself as a slightly less negative substituent constant for the OH group. Also the value of 0.12 [46] for the σ constant for a meta methoxy substituent is equal to the σ constant for a meta hydroxy substituent.

A consideration of the linear relationship between half-wave reduction potentials and σ^- substituent constants shows that a linear correlation between the rate of chromium(II) reduction of the substituted benzonitrile complexes and the ease of reduction of the substituted benzonitrile ligands can be obtained.

The activation energy for the reduction of pentaamminecobalt(III) complexes thought to be proceeding by a radical ion mechanism is usually fairly small. As shown in Table 12 the activation energy for the reduction of the 3-cyanophenol complex is slightly higher than expected for a radical ion mechanism. This, however, may only be a reflection of the fact that the 3-cyanophenol ligand is more difficult to reduce than, for example, the terephthalonitrile ligand. It has been proposed [3] that the

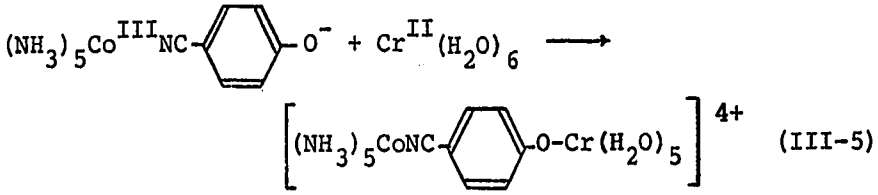
reduction of the terephthalonitrile complex proceeds via a radical ion mechanism.

The arguments concerning the relationship between the rate of reduction of the 3-cyanophenol complex indicate that a radical ion or superexchange mechanism may be operating. These two mechanisms cannot be separated on the basis of ligand reducibility.

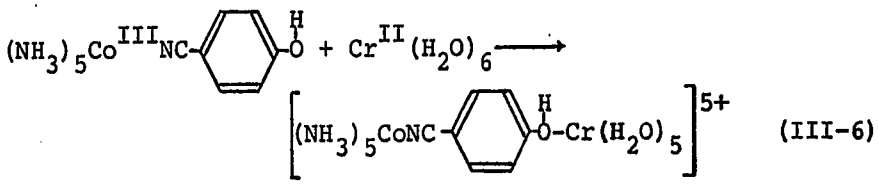
It is interesting to note that the reduction of the benzonitrile complex of cobalt(III) has a rate constant that is over two times larger than 0.017 M^{-1} sec^{-1}, the rate constant for reduction of the acetonitrile complex of pentaamminecobalt(III). The latter may be regarded as the outer sphere limit for the reduction of nitrile complexes. The benzonitrile complex, however, cannot be reduced by an inner sphere mechanism as it does not have the required site for attack by the reductant. As can be seen from Figure 5 the rate of reduction of this complex fits into the relationship between the rate and the reducibility of the ligand. Therefore, it appears that the reducibility of the ligand is important for the reduction of a complex that cannot be operating by an inner sphere mechanism.

The data tabulated in Table 9 also shows that the rate of reduction of 3-cyanophenol complex is independent of the hydrogen ion concentration. This is reasonable for a mechanism involving reduction of the ligand since loss

of the proton from the hydroxy group will increase the negative charge on the ligand and should decrease the reducibility of the complex relative to the protonated form. If the formation of a precursor complex is very important in the reduction the rate might be expected to increase for the unprotonated complex. This is because the coordinated 3-cyanophenoxide ion would form a more stable complex (III-5) with the reductant than would the coordinated 3-cyanophenol ligand (III-6).



(III-5)



(III-6)

The rate being independent of the acid concentration indicates again that the ease of reduction of the ligand is more important than the stability of the bridged complex for these nitrile systems at least.

The outer sphere radical ion mechanism does explain the experimental data fairly well as far as the larger part of the reduction of the 3-cyanophenol complex is

concerned. However, there is still a small amount, approximately 7%, of the reaction that proceeds with ligand transfer and can be considered as an inner sphere path. The ligand reducibility arguments used previously for the outer sphere radical ion mechanism can be applied equally as well to an inner sphere radical ion mechanism for the small inner sphere path. However, of the three mechanisms proposed for inner sphere reduction with remote group attack only the direct exchange mechanism can be eliminated; the direct exchange rate of reduction would be expected to be independent of the ligand reducibility as the reducing electron is at no time in a ligand orbital. The radical ion and superexchange mechanisms differ only in the lifetime of the ligand radical and therefore are both dependent on the reducibility of the ligand.

The 3-cyanophenol complex and the 4-cyanophenol [3,47] complex have similar amounts of the reaction proceeding by an inner sphere path, approximately 7%. This differs somewhat from the amount of ligand transfer observed in the chromium(II) reduction of the terephthalonitrile complex [3], where no ligand transfer occurs. The differences in the amount of ligand transfer may indicate that as the reducibility of the ligand decreases the inner sphere bridging mechanism may provide an energetically more favourable path. This path may be more favourable because the reducibility of the ligand is increased when chromium(II) is

bonded to the remote group. The ligand may become more reducible because of the increase in positive charge brought about by bonding to chromium(II). Therefore the greater the ease of reduction of the ligand the lesser the amount of the reaction proceeding by a ligand transfer mechanism. However, in comparing the cyanophenol complexes and the terephthalonitrile complex the differences in the basicities of the remote group must be considered. This may also be a factor in explaining the different amounts of ligand transfer.

In an outer sphere electron transfer the rate determining step is the transfer of the electron from the reductant orbital to a vacant oxidant orbital. Clearly the energy of the orbital into which the electron is being transferred is very important. One might possibly expect that the lower the energy of this orbital the greater the rate of reduction. Similarly in an outer sphere radical ion or superexchange mechanism the energy of the ligand orbital receiving the reductant electron is very important. The lower the energy of this orbital the greater the rate of reduction. The energy of this ligand orbital is necessarily fairly high otherwise the reduced ligand, the radical ion, would be a stable state and the electron would not be transferred to the oxidising centre. The visible and ultraviolet spectra of a series of substituted benzonitrile complexes of cobalt(III) together with their

rates of chromium(II) reduction are given in Table 14. The long wavelength absorptions with small extinction coefficients (approximately 100) can be considered as d-d electron transitions taking place exclusively on the cobalt(III). However, a correlation between the energies of these transitions and the rate of chromium(II) reduction was not obtained. The shorter wavelength absorptions in the electronic spectra of the benzonitrile complexes which all have extinction coefficients of $>10^3$ can be considered as charge transfer bands or ligand absorption bands with a $\pi \rightarrow \pi^*$ origin. Also a clear correlation between the energies of these transitions and the rate of chromium(II) reduction was not obtained. Clarke and Ford [27] have shown that there is a correlation between the wavelengths of the absorptions in the electronic spectra of substituted nitrile complexes coordinated to ruthenium(II) and ruthenium(III) and the Hammett σ constants of the substituents on the nitriles. They observed that the more electron withdrawing the group, as estimated from the Hammett σ constants, the longer the wavelength of the absorption maxima. They suggested that this was indicative of a metal to ligand charge transfer band as an assignment for these absorptions. Metal to ligand charged transfer bands showing similar susceptibility towards substituents have been observed with pentaammineruthenium(II) complexes of substituted pyridines.[48] However, no such

TABLE 14

Electronic Spectra of a Series of Benzonitrile Complexes

Ligand	k(25°C) M^{-1} sec^{-1}	Hammett σ Constant	Absorption Maximum cm^{-1} (Extinction Coefficient M^{-1} sec^{-1})
3-Cyanophenol [a]	4.17×10^{-2}	0.12	21,300 (78.6) ; 33,200 (3.53×10^3) 42,700 (1.33×10^4)
4-Cyanophenol [a]	2.96×10^{-2}	-0.11	21,200 (95.5) ; 39,000 (2.16×10^4)
4-Cyanobenzoic acid [a]	0.282	0.73	21,200 (80.4) ; 30,100 (102.2) 34,800 (2.74×10^3) ; 40,500 (2.36×10^4)
Terephthalonitrile [b]	0.92	0.91	21,300 (78.5) ; 30,400 (86.5) 39,200 (1.89×10^4) ; 42,000 (2.33×10^4)

(a) Spectra observed in dilute $HClO_4$

(b) Spectra observed in H_2O

correlation was observed for pentaamminecobalt(III) complexes of substituted benzonitriles. Without a strict assignment of the absorption bands in the ultraviolet spectra no definitive conclusions can be drawn. However, it appears that the absorption bands are mainly due to the ligand itself with some perturbation due to coordination to the cobalt(III) centre.

CHAPTER IV

C O N C L U S I O N S

There are numerous examples of the effect on the chemical properties of a ligand by coordinating the ligand to a pentaammminecobalt(III) moiety. One of the most easily studied effects is the change in acidity of a ligand upon coordination. For the nitrogen bonded isomers of the sulphamato [49] ($NH_2SO_3^-$), formamido [3] (NH_2CHO) and benzamido [24] complexes of pentaamminecobalt(III) the pK_a of the NH_2 protons is decreased by more than 10 pK units after coordination. The effect can be generally attributed to the electron withdrawing effect of the $(NH_3)_5Co^{3+}$ group and attenuates in the expected way as the acidic group is further removed from the metal ion centre. The electron withdrawing effect of the metal is also expected to increase the susceptibility of coordinated ligands to nucleophilic attack. An example of this is found in the effect of the coordinated transition metal ion on the rate of hydrolysis of coordinated nitriles. It has been shown that the rate of hydrolysis of the nitrile group in 2-cyano-1,10-phenanthroline [5] and in 2-cyanopyridine [6] can be greatly enhanced by the presence of Ni^{2+}, Zn^{2+} and Cu^{2+} ions. The metal ion is coordinated to the pyridine-type nitrogen atom in these ligands and facile alkaline hydrolysis is observed at the free nitrile group. The

rate of hydrolysis of the coordinated ligand is of the order of 10^6 times greater than the rate of hydrolysis of the uncomplexed ligand. The coordination of the 3- and 4-cyanophenol ligands to $(NH_3)_5Co^{3+}$ group increases the reactivity of the nitrile group towards alkaline hydrolysis. The rate of hydrolysis of uncoordinated benzonitrile was found to be 8.2×10^{-6} M^{-1} sec^{-1} at 25.6°C.[9] Therefore coordination resulted in an increase in the rate of alkaline hydrolysis of the order of 10^6. Presumably the electron withdrawing power of $(NH_3)_5Co^{3+}$ increased the susceptibility of the nitrile carbon atom to attack by a nucleophile.

The rate of alkaline hydrolysis of the 3- and 4-cyanophenol cobalt(III) complexes was found to be first order with respect to hydroxide ion. A microanalysis and an electronic, infrared and pmr spectroscopic analysis of the products of the benzonitrile hydrolysis were found to be consistent with the formation of the N-bonded carboxamide complex. The formation of this N-bonded isomer is of interest as it appears that the hydrolysis of the nitrile complexes is a general method of preparing the N-bonded carboxamido complexes.

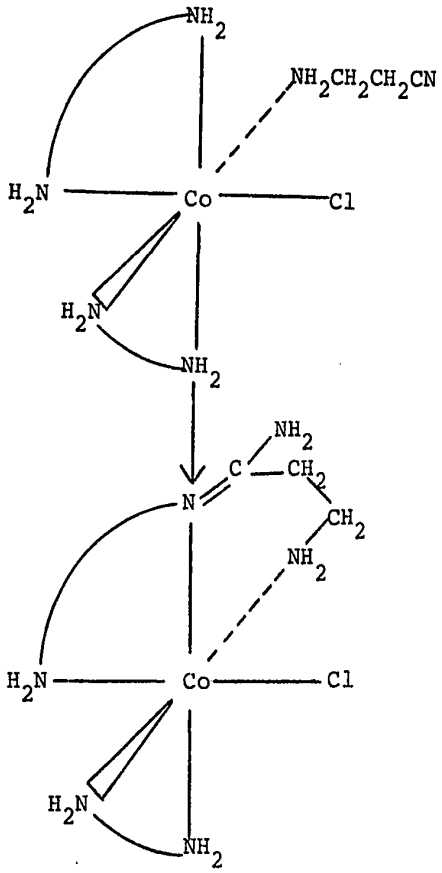
Both Wiberg, and Cohen and Jones have found linear free energy relationships between the rates of hydrolysis of a series of substituted nitriles and the Hammett σ constants of the substituents. A similar relationship has

been observed in this study with more electron withdrawing substituents increasing the rate as expected for nucleophilic attack of hydroxide ion at the coordinated nitrile group. The correlation observed here could be readily extended to include many other substituents for which σ constants have been calculated. Examples of the ligands whose rate of nitrile hydrolysis after coordination might be studied are 4-cyanobenzoic acid, 4-cyanobenzaldehyde, terephthalonitrile and isophthalonitrile. These would provide a wide range of Hammett σ constants. In particular the hydrolysis of the 4-cyanobenzaldehyde and the terephthalonitrile complex would be expected to be much faster than the cyanophenol complexes as they have large positive Hammett σ constants of 1.13 and 0.96 respectively.

It has been shown [5] that the rate of alkaline hydrolysis of 2-cyano-1,10-phenanthroline is greatly enhanced by the presence of Ni^{2+}, Zn^{2+} or Cu^{2+} ions. The enhancement, it is argued, is due to a more favourable activation entropy associated with the bonding of the developing imino ion to the metal. In the cyanophenol systems the imino ion formed during hydrolysis is already bonded to the metal and a similar more favourable activation entropy was found.

It may be of interest to show whether or not the more favourable entropy is associated with the coordination of the imino ion or not and also the possible electronic effect of the metal centre on the remote nitrile group.

Coordination of the 2-cyano-1,10-phenanthroline to tetraamminecobalt(III) would provide a complex with no site for coordination by the imino ion formed on hydrolysis of the nitrile group. However, this complex may be difficult to prepare because of the steric interaction between the nitrile group and the ammonia ligands on cobalt(III). However, coordination of 2-cyanopyridine to pentaamminecobalt(III) would provide a similar system for study. This complex would be expected to form fairly easily since the 2-methylpyridinepentaamminecobalt(III) complex has been prepared.[50] However, it has been observed [51] that cis-$[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$ reacts in near neutral or basic solution to give a purple complex $[Co(en)(NH_2CH_2C(NH_2)=NCH_2CH_2NH_2)Cl]^{2+}$ where one end of a bidentate ethylenediamine ligand has lost a proton and condensed with the NH_2CH_2CN group, followed by rearrangement to give the product (IV-1). Therefore the possibility exists that this type of intramolecular nucleophilic attack may occur in the 2-cyanopyridine complex of $(NH_3)_5Co^{3+}$ with one of the ammino groups as the potential nucleophile. However, the coordinated ethylenediamine protons are more acidic, by about 3 pK units, than the ammonia protons and formation of the NH_2^- intermediate will be less favored in the ammonia system.



(IV-1)

In any mechanistic discussion of electron transfer reaction the analysis of the reduction products is very important. It must be emphasised that the kinetic parameters of the reduction cannot be relied upon in the same way as product analysis to indicate the mechanism.

The rate of the chromium(II) reduction of the 3-cyanophenol cobalt(III) complex was found to be first order with respect to chromium(II) and independent of the hydrogen ion concentration. Thus the phenoxide complex is not reactive.

The mechanism of the reduction of 3-cyanophenolpentaamminecobalt(III) consists of two paths, a small path in which ligand transfer takes place and a much larger path in which no ligand transfer can be detected. A normal outer sphere mechanism where the electron is transferred directly from the reductant to the oxidant may be postulated for the large path. However, small changes in the nitrile ligand coordinated to cobalt(III) causes changes in the rates of reduction of these complexes. This is not expected for an outer sphere mechanism. Also the activation parameters for the reduction of this complex are somewhat different than those expected for a true outer sphere process.

A totally inner sphere radical ion or superexchange mechanism may be postulated for the reduction of the complex followed by partial hydrolysis of the chromium(III) ligand transfer complex. This mechanism is consistent with the correlation between the rate of reduction and the half-wave potentials of reduction of the ligand and therefore the ligand's reducibility. Also the activation parameters are similar to those of established radical ion reductions. However, this inner sphere mechanism is not acceptable as the chromium(III) ligand transfer complex is thought to be stable towards hydrolysis [3] and therefore much more of the ligand transfer complex is expected as a product. However, it is likely that this

mechanism isin fact operating for a small part of the reaction producing the approximately 10% of ligand transfer observed. It cannot be decided whether the inner sphere path is a radical ion or superexchange mechanism from the ligand reducibilities.

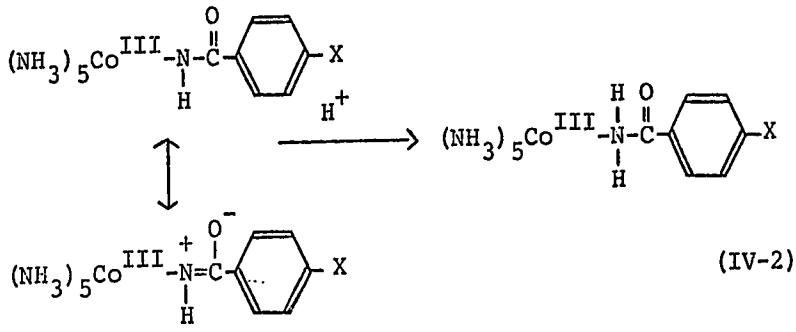
As neither of the two previous mechanisms sufficiently explain the experimental data the outer sphere radical ion or superexchange mechanisms were postulated and seem to be the most likely explanation for the larger of the two reduction paths. In these cases the electron is transferred from the reductant directly into a ligand orbital without bridge formation. The reducibility of the ligand for both of these mechanisms is important and thus both fit in with the experimental correlation between the rate of reduction and ligand reducibility. Also the activation parameters are similar to those of established radical ion reductions. The outer sphere radical ion or superexchange mechanism for electron transfer for this type of organonitrile ligand is supported by the rate of reduction of the benzonitrile cobalt(III) complex. As previously noted this ligand does not have the remote group required for the formation of the precursor complex with the reductant and thus cannot be reduced by an inner sphere mechanism. The rate of reduction of the benzonitrile complex is 4.27×10^{-2} M^{-1} sec^{-1} which is greater than the outer sphere limit. Also the rate of reduction fits in well with the linear rela-

tionship with the rate of reduction and the Hammett σ^- constants and thus the reducibility of the ligand.

The relationship observed in this work between the reducibility of the ligand and the rate of electron transfer is a strong indication that a radical ion or superexchange mechanism is operating. However, this relationship has only been defined in a few systems. It would be of interest to extend the series of ligands studied to those with other substituents which are potential sites for remote attack and have known Hammett constants. Such substituents are the aldehyde, on which a preliminary study has been carried out [3], the acid group (COOH) which is being studied at present and the meta nitrile group. The 4-cyanobenzaldehyde complex is expected to have a rate of reduction greater than the terephthalonitrile complex as its σ^- constant value is 1.13. The isophthalonitrile complex should have a rate of reduction that falls in the middle of the series so far studied as its σ constant value is 0.61. Other substituents of interest that have known σ constant values are the methoxy group (OCH_3), which is expected to have a rate of reduction similar to the phenol, and an ester group (CO_2R). When R in the ester function is a methyl group σ^- is 0.76 for a para substituent and σ_m is 0.36 for a meta substituent.

Another similar series of ligands with a different group coordinated to the cobalt(III) species could be

studied to see if the reducibility versus rate correlation holds for other ligands. In this regard the substituted benzamidopentaamminecobalt(III) complexes may be useful. They are similar to the nitriles and the carboxamido group is thought to participate in a radical ion mechanism in the isonicotinamide complex. Also they are easy to prepare by hydrolysis of the corresponding nitrile cobalt(III) complex. Benzamido complexes are of special interest for a radical ion or superexchange electron transfer since a protonated benzamide breaks the conjugation between the aromatic ring and the oxidant (IV-2). This could have the effect of trapping the electron in the aromatic system and perhaps allowing the detection of a radical ion intermediate.



(IV-2)

However, the disadvantage of the benzamido complexes is that they have a site, the carbonyl oxygen, for possible adjacent attack by the reductant. This would increase the problems in determining the mechanism of the reduction.

It is interesting to note that for complexes oper-

ating by a radical ion or superexchange mechanism, the amount of ligand transfer and thus inner sphere reaction could be increased perhaps by increasing the basicity of the remote group, such as an amino group ($-NH_2$). However, the rate of reduction of such a complex would decrease since the NH_2 group has a large negative σ^- constant and therefore the reducibility of the ligand would be decreased. Thus a series of complexes can be envisaged where the amount of ligand transfer increases but the rate of reduction decreases. In this context any mechanistic conclusions based on rate data would be entirely invalid.

An important question relating to the reduction of the cyanophenol cobalt(III) complexes is whether or not coordination of the cyanophenol ligands to the pentaamminecobalt(III) moiety increases the reducibility of the ligand. In this particular system under discussion the electron on the reduced ligand reduces the oxidant, cobalt(III). However, any increase in the ease of reduction of the ligand by coordination may be due to a σ effect of the metal ion. This would be of great interest as a means of increasing the ease of reduction of various compounds by coordination to a transition metal ion.

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