A DISSERTATION

entitled

A KINETIC STUDY OF THE INDUCED AQUATIONS
OF SOME CHROMIUM(III) COMPLEXES

by

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PREFACE

The studies described in this dissertation were undertaken in the School of Molecular Sciences of the University of Warwick between October, 1966 and October, 1970. The work is original and the author's own, except where specific mention is made to the contrary. None of the information contained herein has been submitted either wholly or in part to this or another University for the award of a degree.

The author is indebted to his supervisor, Dr. Peter Moore, for his constant advice and encouragement, to his colleague, David Benton, Esq., for many helpful discussions, and to Professor V.M.Clark for providing research facilities. The award of a Research Associateship by the University of Warwick is gratefully acknowledged.

Parts of the work contained in this thesis have been published, or accepted for publication, in the scientific literature, with the following references :

T.C.Matts and P.Moore,	Chem. Comm., 1969, 29.	
idem	,	J. Chem. Soc.(A), 1969, 219.
idem	,	ibid. , 1969, 1997.
idem	,	ibid. , in press, paper no. 0/961.

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ABBREVIATIONS

S.I. units are used in this thesis unless alternative symbols are
defined in the following list :

exp	exponential function.
G	Gibb's free energy.
h	Planck's constant.
K	Boltzmann's constant.
kcal	kilocalorie = 4184 J.
R	gas constant per mol.
ESD	estimated standard deviation.
I	ionic strength.
M	mol l^{-1} concentration.
λ	wavelength.
E_M	molar extinction coefficient (units of $M^{-1}cm^{-1}$).
ΔH^o	standard enthalpy change.
$\Delta H^{\ddagger}$	activation enthalpy change.
$\Delta S^{\ddagger}$	activation entropy change.
k	rate constant.
k_{obs}	observed first-order rate constant.
K (with super- or subscript)	equilibrium constant.
pK_a	$-\log_{10}$ (acid dissociation equilibrium constant).
bipy	2,2'- bipyridine.
dien	diethylenetriamine.
EDTA	ethylenediaminetetra-acetic acid.
en	ethylenediamine.
tren	2,2',2''-triaminotriethylamine.
Kel-F	polyfluorotrichloroethylene.
PTFE	polytetrafluoroethylene.

SUMMARY

The original intention of the work was to garner evidence for or against the participation of a D process in the substitution reactions of Cr(III) complexes. The kinetics of the aquation of $Cr(H_2O)_5N_3^{2+}$ induced by nitrous acid were studied as an adjunct to stoicheiometric experiments using the same reaction, in which the possible five co-ordinate intermediate, $Cr(H_2O)_5^{3+}$, was sought. The rapid reaction rate was found to be first-order in /complex/, /H⁺/, and /HNO₂/, and much faster in the presence of chloride ion. High concentrations (2 - 5M) of added anions were used in the stoicheiometric experiments in an attempt to trap the intermediate as mono-acidopenta-aquochromium(III) complexes. Low concentrations of such species were, indeed, detected, but the discrimination of the postulated intermediate for the anions and against solvent water was small. The discrimination factors obtained for Cl⁻ and Br⁻ were much lower than those reported by another worker during the spontaneous acid hydrolysis of $Cr(H_2O)_5I^{2+}$, and indicate that, either the _trans_-labilising ability of the iodo-ligand was responsible for the incorporation of Cl⁻ and Br⁻ in the previous work, or that different intermediates are involved in the spontaneous and induced aquations. Though the evidence tends to favour the participation of a highly reactive intermediate in the induced reaction, the data are not totally inconsistent with an interchange mechanism. Due to the inconclusive nature of the results obtained in the competition studies, and the uncertainty that other approaches would provide definitive evidence, attention was turned to an interesting observation that was made during preliminary experiments to the stoicheiometric work.

Nitrous acid was found to be an efficient catalyst for the aquations of halo-aquochromium(III) complexes in acidic aqueous media. Other oxyacids have little or no effect at low pH values. The kinetics of aquation of $Cr(H_2O)_5Br^{2+}$ in the presence of HNO_2 were studied in detail.

Reaction rates are first-order in $[$complex$]$ and $[HNO_2]$ and are proportional to the reciprocal of $[H^+]$ at high acid concentrations. At lower acidities, limiting rate behaviour is indicated. The possibilities of an ion-pair mechanism or direct attack by a nitrosating species on the leaving group were excluded, and transient nitrito-intermediates, formed by the rapid O-nitrosation of an aquo-ligand, are thought to be involved in the catalysis mechanism. Studies of the isomers cis- and trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$ showed that the aquation of only the cis-isomer is catalysed by HNO_2, indicating that a cis-halo-nitritochromium(III) intermediate is labile with respect to loss of halide ion. Possible explanations for this phenomenon are advanced. Preparative work re-inforces the conclusions derived from kinetic studies, and several new nitritochromium(III) complexes are reported.

The acid hydrolyses of nitritochromium(III) complexes were found to be both rapid and acid catalysed, in contrast to a previous report. The same rate law is applicable to all five complexes studied and contains terms in both $[H^+]$ and $[H^+]^2$. The rate constant independent of acid concentration appears to be very small. A mechanism involving singly and doubly protonated intermediates is suggested. The reactions are thought to proceed without chromium-oxygen bond cleavage because of their rapid nature, their low $\Delta H^{\ddagger}$ values, and by analogy with the formations of nitrito-complexes, which are believed to avoid Cr-O fission.

Much of the kinetic work involved in these studies was carried out using the stopped-flow method. Modifications to a Gibson-Milnes stopped-flow spectrophotometer are described which allow the instrument to be used with highly acidic and other corrosive solutions.

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CHAPTER I

GENERAL INTRODUCTION

1-1. Chemical Background

The existence of many excellent texts[1-5] and reviews[6-11] on the reactions of metal complexes renders unnecessary a complete discussion of the concepts underlying this field of chemistry. However, certain points will be examined, insofar as they impinge on the studies contained in this dissertation.

Early studies in co-ordination chemistry were rationalised by Werner's concept[12] of a metal complex, which can be considered as a central metal ion surrounded by a characteristic number of electron-donating molecules or ions. We can consider the metal ion as an acid, and the attached groups, or ligands, as bases, using the theory of G.N. Lewis[13] as to acid-base character. The thermodynamic stabilities of metal complexes have been much studied, using Bjerrum's theory of stepwise formation[14] as a basis. Methods and results are well documented[4a, 15, 16]. Much effort has also been devoted to dynamic processes, especially during the last two decades.

Simple reactions of co-ordination complexes can be assigned to one of three broad categories:

    <u>1.</u>   Substitution processes

    <u>2.</u>   Redox processes

    <u>3.</u>   Reactions of co-ordinated ligands.

The total mechanism of a reaction may involve processes fitting into more than one of the above categories. For instance, an "inner-sphere" redox reaction involves substitution in addition to electron transfer. Protonation or deprotonation of a co-ordinated ligand, a category <u>3</u> process, often occurs in connection with substitution.

Also the following reaction:

$$Co(NH_3)_5{}^*OH^{2+} + N_2O_3 \rightleftharpoons Co(NH_3)_5{}^*ONO^{2+} + HNO_2$$
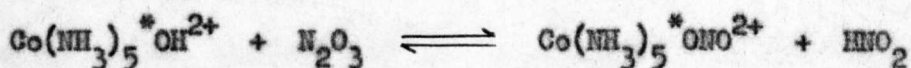
might be considered as substitution, since the nature of the ligand is

totally changed.   However, the reaction must be placed in category 3 since the Co-*O bond remains intact, as proved by ^{18}O tracer studies[17]. The formations and dissociations of nitrito-complexes are particularly relevant to this work, and will be discussed in greater detail later. Another category 3 process, the oxidation of a co-ordinated azido group, is also pertinent to this study, and will be mentioned in due course. Reactions of co-ordinated ligands form a very diverse subject, which is not 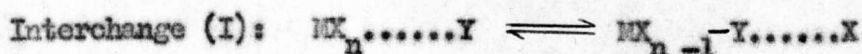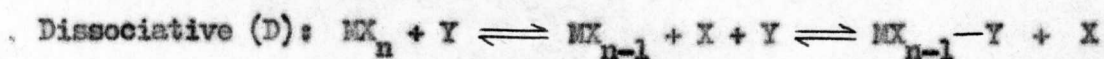well documented.   Some reviews are, however, helpful[18, 19].   In contrast, redox processes are well reviewed[1a, 3a, 20, 21].

Taube[22] has defined metal complexes as either "labile" or "inert" with regard to the rates of their substitution processes.   Complexes whose reactions are complete within one minute, referred to room temperature and concentrations of ca. 0.1M, are said to be labile.   Other complexes are classified as inert, though some borderline cases do exist, since the division is purely arbitrary.

Gross trends in the reactivity of metal complexes can be predicted by a simple electrostatic theory, assuming point charges and dipoles, but subtle variations exist, especially with transition metal complexes, which depend on the electronic configuration of the metal ion, the structure of the complex, and the nature of the ligands.   The anomalies can be largely resolved by the application of the Crystal or Ligand Field theories, which are fully discussed by Basolo and Pearson[1b, c].   For instance, the inertness of octahedral d^3 (e.g. Cr(III)), low-spin d^6 (e.g. Co(III), Rh(III)), and square-planar d^8 (e.g. Pt(II), Pd(II)) complexes can be explained using Crystal Field Theory.   Considering Cr(III), on simple electrostatic grounds, we could consider that its compounds might be somewhat more labile than those of Al(III), since both metal ions have the same charge, but the latter has a smaller radius.   However, octahedral Cr(III) complexes experience an extra stabilisation energy, due to the crystal field splitting of the d-orbitals.   Some crystal field stabilisation energy will be lost during a reaction in proceeding to

either a five or seven co-ordinate transition state[1c]. This effect enhances the activation energy required for the process, and results in a very slow reaction rate.

Basolo and Pearson[1d] have extended the nomenclature developed by Hughes and Ingold[23] to describe different types of organic processes, to facilitate its application to the substitution reactions of metal complexes. A rather more useful approach, however, has been evolved by Langford and Gray[2a]. They suggest three possible pathways for a substitution reaction in solution:

Dissociative (D): $MX_n + Y \rightleftharpoons MX_{n-1} + X + Y \rightleftharpoons MX_{n-1}-Y + X$

Associative (A): $MX_n + Y \rightleftharpoons MX_n-Y \rightleftharpoons MX_{n-1}-Y + X$

Interchange (I): $MX_n \ldots \ldots Y \rightleftharpoons MX_{n-1}-Y \ldots \ldots X$

The interchange mechanism is visualised as an exchange of ligands between the inner and outer co-ordination spheres of a complex. The inner sphere consists of ligands which are strongly bound to the metal ion, while the outer sphere consists chiefly of solvent molecules held by feeble interactions. Non-solvent molecules and ions may also be weakly bound in the outer sphere. In the D process, bond breaking is the dominant factor determining the energetics of the reaction, while bond making is important in the A process. The I mechanism may be divided into two sub-categories, I_d and I_a, depending on the relative importance of bond breaking and bond making in the transition state. The D, I_d, I_a and A processes correspond closely to the $S_N 1$ (lim), $S_N 1$, $S_N 2$, and $S_N 2$ (lim) categories, respectively, as used by Basolo and Pearson[1d].

In both the D and A mechanisms, a definite reaction intermediate is envisaged, even though this may be metastable with respect to reactants and products, and can seldom be isolated. No detectable intermediate is postulated for an I mechanism. The course of the three reaction schemes can best be illustrated using the familiar transition state theory free energy versus reaction co-ordinate plots (Figures 1 and 2).

FIGURE 1

Free energy profile for both

A and D mechanisms
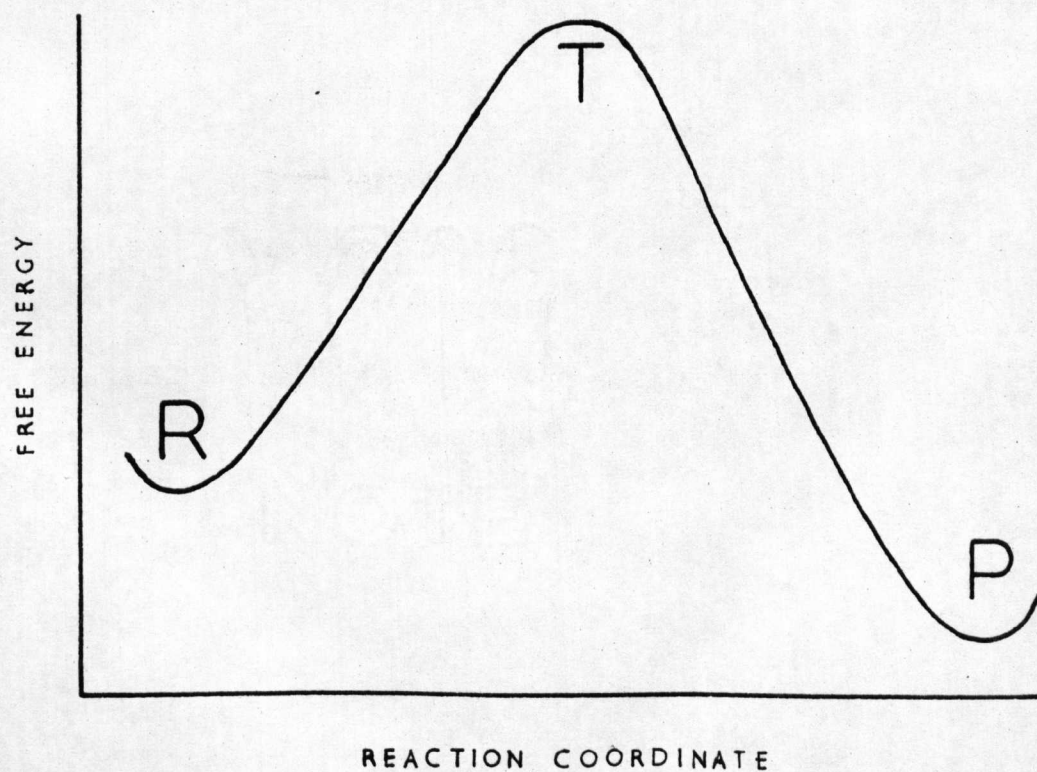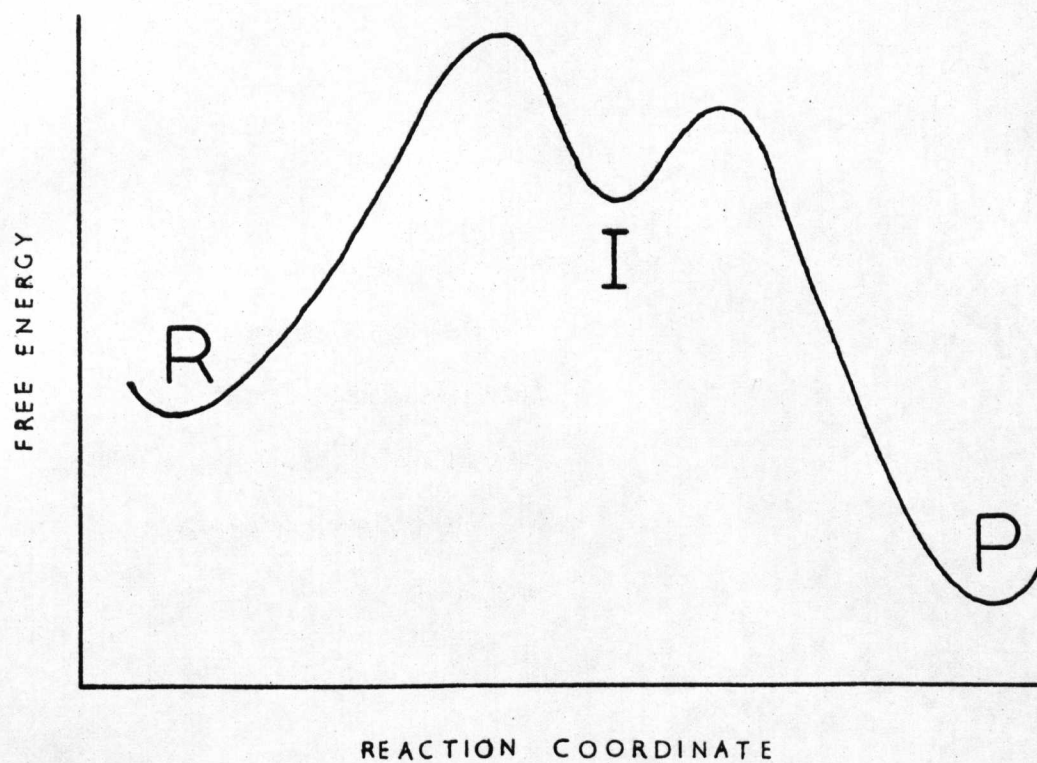
R   Reactants, MX + Y

I   Intermediates, XMY for A process

    M + X + Y for D process

P   Products, MY + X

FIGURE 2

Free energy profile

for an I mechanism

R   Reactants, MX + Y

T   Activated complex, X.....M.....Y

P   Products, MY + X

FREE ENERGY

R

I

P

REACTION COORDINATE

FREE ENERGY

R

T

P

REACTION COORDINATE

The substitution reactions of octahedral complexes usually proceed by a dissociative mechanism, while those of complexes having a lower co-ordination number normally involve association. Some exceptions to the dissociative rule for octahedral complexes have recently come to light, notably the work by Taube and co-workers[24] on the reaction of NO with $Ru(NH_3)_6^{3+}$. Associative character in the reactions of some $Cr(III)$[25], $Rh(III)$[26], and $Fe(II)$[27] complexes has been suggested. The more open structure of complexes with co-ordination numbers less than six is believed to encourage associative processes, though steric hindrance can sometimes promote dissociative activation[1e].

The chief line of evidence for a dissociative mechanism in the substitution reactions of octahedral complexes is the lack of dependence of the reaction energetics on the entering group, with the notable exception of the hydroxide ion. Subsidiary criteria arise from the decrease of the reaction rate with increase of the charge on the complex, the increase of rate with steric crowding within the complex, and the close correlation of reaction rate with leaving group binding. The last factor can best be illustrated by means of a linear free energy plot[28a], e.g. for the process:

$$Co(NH_3)_5 X^{2+} + H_2O \rightleftharpoons Co(NH_3)_5 H_2O^{3+} + X^-$$
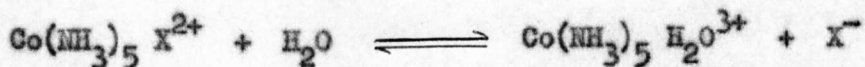
If the mechanism of the acid hydrolysis, or aquation, is identical for different ligands X^-, then $\Delta G^{\neq}$ will correlate linearly with ΔG° for the reaction. Hence a straight line plot should be obtained for log k (where k is the rate of acid hydrolysis) versus −log Q (where Q is the formation equilibrium constant at the same temperature, expressed in terms of concentration rather than activity). Much data is available where X is a monovalent anion and, indeed, a good linear relationship is observed (Figure 3)[29]. Moreover, the slope of the line is accurately 1.0, suggesting that the environment of X in the transition state, bears a great resemblance to that in the product, as expected for a dissociative

Plot of $\log_{10} k$ (acid hydrolysis rate) versus
$-\log_{10} Q$ (formation constant) for
acidopenta-amminecobalt(III) complexes.
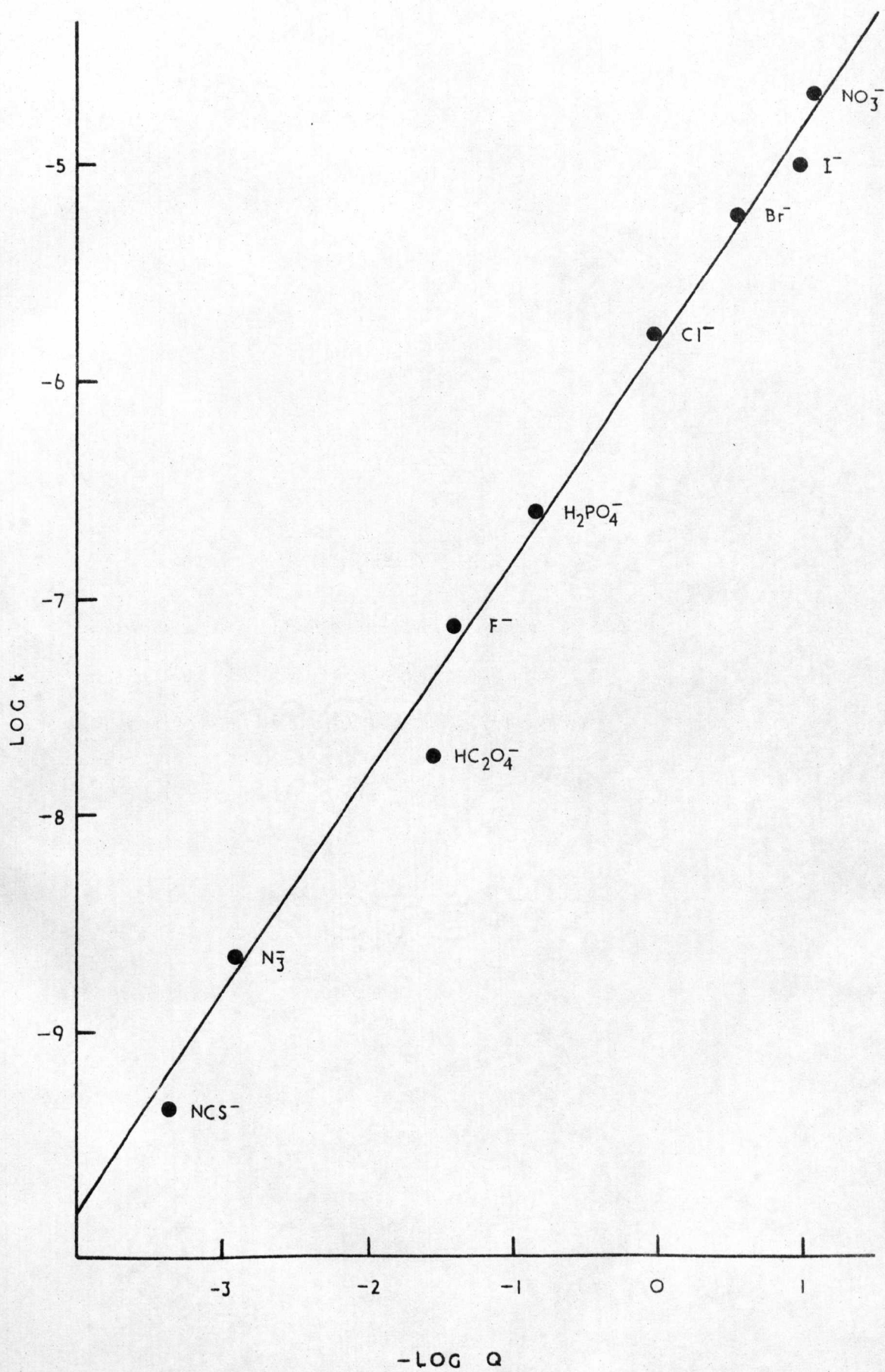
process. A similar free energy relationship is obtained for the equation of acidopenta-aquochromium(III) complexes[30]. However, the slope of the line is only 0.56, which suggests that the leaving group is not completely dissociated in the transition state.

The anomalous effect of hydroxide ion in substitution reactions at octahedral centres has caused much controversy. The base hydrolysis of a complex in aqueous solution, despite being first order in hydroxide ion concentration, is now generally accepted as involving a dissociative 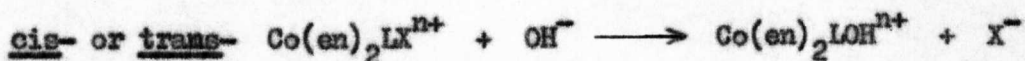conjugate base mechanism[31], rather than an associative process. There are several lines of evidence,[1c, 32, 33] but perhaps the most persuasive is the work on reactions of the type:

cis- or trans- $Co(en)_2LX^{n+}$ + OH^- $\longrightarrow$ $Co(en)_2LOH^{n+}$ + X^-

The values of the isomeric product distributions and the fact that these values do not depend on the nature of the leaving group X^- support a dissociative mechanism involving a trigonal-bipyramidal intermediate. The work has been reviewed by Basolo and Pearson[1f]. A conjugate base mechanism is normally only important at high pH for ammine or amine complexes. However, the presence of more acidic groups in a complex, such as the aquo-ligand, often renders the conjugate base mechanism significant even at a quite high acid concentration. To quote an example relevant to this study, the aquation of the bromopenta-aquochromium(III) ion involves a conjugate base path contributing 24% of the observed rate at 318 K, in 1M $[H^+]$ [34].

Acid hydrolysis reactions of octahedral complexes are normally pH independent, providing that the solutions are sufficiently acid to ensure that conjugate base formation is negligible. However, strongly basic ligands can sometimes be labilised by protonation, resulting in acid catalysis. This effect has been observed in Co(III) and Cr(III) systems[35-41] involving such ligands as $-NO_2^-$, F^-, N_3^-, SO_4^{2-}, and $-CN^-$. In this study, the dramatically acid catalysed aquations of O-bonded nitrito-complexes of Cr(III) are demonstrated, and further discussion on this topic will be presented later.

That the substitution processes of octahedral complexes usually involve dissociative control is not too difficult to demonstrate, but the distinction between a D and an I_d mechanism, in the absence of an isolable intermediate, is by no means straightforward. The distinction is particularly relevant to this work since the question of the existence of the five co-ordinate intermediate $Cr(H_2O)_5^{3+}$ provided the initial stimulus for this study. C.H. Langford has been particularly active in defining criteria to distinguish D and I_d mechanisms[2a] and in reviewing the related evidence[2b, 8, 42, 43]. To be capable of detection, an intermediate must be able to exist for a sufficient time to discriminate between species in the bulk solution, or, at the very least, survive rearrangement of its solvation shell to selectively react with a species in the outer sphere. Hence the intermediate must be stable enough to withstand several collisions with solvent and other non-reacting molecules.

There appear to be two general methods of detecting intermediates of reduced co-ordination number in the reactions of octahedral complexes:

(a)   Kinetic

(b)   Stoicheiometric

A good example of method (a) is the now classical study by Haim and Wilmarth[44, 45] on the anation of $Co(CN)_5H_2O^{2-}$ by N_3^- and SCN^-. A genuine D process would lead to the following mechanism for the anation reaction:

$$Co(CN)_5H_2O^{2-} \xrightarrow[\quad k_2 \quad]{\quad k_1 \quad} Co(CN)_5^{2-} + H_2O$$

$$Co(CN)_5^{2-} + X^- \xrightarrow{\quad k_3 \quad} Co(CN)_5X^{3-}$$
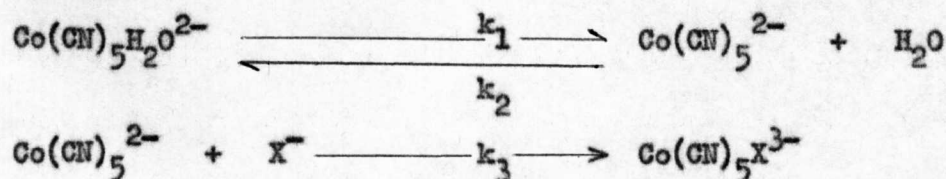
This mechanism would exhibit the following rate law:

$$k_{obs} = k_1[X^-] / ([X^-] + k_2/k_3)$$

If $[X^-]$ were large compared to k_2/k_3, a rate independent of $[X^-]$ would be expected. Evidence for a limiting anation rate at high anion concentration was indeed observed, the calculated value of which was independent of the identity of the anion, but agreed very well with the water exchange rate determined by an ^{18}O tracer method. Since ion-pairing would be unlikely,

due to the like nature of the charge on both complex and substituting anion, an intermediate must be formed during the reaction which exists sufficiently long to discriminate in favour of entry of an anion, and against the re-entry of a solvent molecule. Similar kinetic evidence supports the existence of other five co-ordinate intermediates, such as $Co(NH_3)_4SO_3^+$ [46], $Co(CN)_4SO_3^{3-}$ [47], and $RhCl_5^{2-}$ [48].

Kinetic evidence for an interchange mechanism is often obtained in the rates of formation of complexes from solvated metal ions, [10,11] if one assumes that Eigen's outer-sphere association mechanism [49] is operative. Consider the following general scheme:

$$MS_n^{x+} + X^{y-} \xrightleftharpoons{K_o} MS_n^{x+} \cdots\cdots X^{y-}$$

$$MS_n^{x+} \cdots\cdots X^{y-} \xrightarrow{k_i} MS_{n-1}X^{(x-y)+}$$
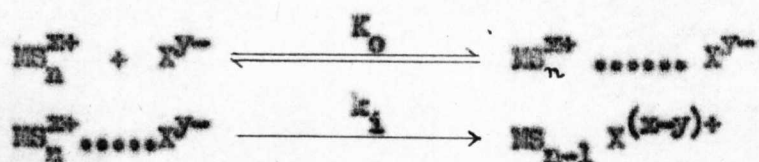
If K_o is small, then $k_{obs} = K_o k_i$. A knowledge of the outer-sphere association constant K_o will enable an estimation of k_i to be made. In a majority of cases, values of k_i are found to be of the same magnitude as, but somewhat less than, the rate of solvent exchange. This is understandable if the transition state involves the interchange of a non-selected species, since the chance of incorporation of a reagent rather than a solvent molecule is purely dependent on their relative population in the outer sphere. Values of k_i have been calculated for the anation of $Co(NH_3)_5H_2O^{3+}$, [50] $\underline{cis}$-$Co(en)_2(H_2O)_2^{3+}$ [51], and $Cr(NH_3)_5H_2O^{3+}$ [52] by such ions as SO_4^{2-}, Cl^-, and SCN^-. In all cases k_i was found to be between 5% and 25% of the water exchange rate, conforming neatly to I_d predictions.

Stoicheiometric methods designed to detect intermediates have been of two kinds:

1. Competition experiments in which a selectivity factor is determined by a comparison of the proportion of products formed in the reaction with the proportion of entering groups present in the original solution.

2. Demonstration of a common intermediate by obtaining identical

   products from the reactions of a wide range of precursors.

Method 1 has been used in the current study and further aspects will be discussed later. As an example of Method 2, Loeliger and Taube[53] have tabulated results from their own and earlier studies of the Hg^{2+} and NO^+ induced aquations of cis- and trans-$Co(en)_2Cl_2^+$, $Co(en)_2(N_3)_2^+$, $Co(en)_2H_2ON_3^{2+}$, $Co(en)_2H_2OCl^{2+}$, $Co(en)_2H_2O\ Br^{2+}$, $Co(en)_2Cl\ Br^+$, and trans-$Co(en)_2Cl\ N_3^+$ ions to show that the ratio of cis and trans products is independent of the leaving group. Sargeson and co-workers[54] have extended the above study to optical isomers and obtained evidence for a trigonal-bipyramidal intermediate. Relevant evidence from the base hydrolyses of Co(III) complexes has been mentioned above[1f].

Perusal of the review by Muetterties and Schunn[55] shows the dearth of stable five co-ordinate species, with the exception of organo-metallic complexes. Other examples involve cyanide ion as a ligand (e.g. $Co(CN)_5^{3-}$, $Ni(CN)_5^{3-}$). These facts could indicate that π-acceptor non-labile ligands may be important in stabilising a five co-ordinate intermediate. Other pentaco-ordinate stable species have been prepared using strained or sterically hindered ligands. Examples include high-spin complexes of divalent metal ions of the first transition series prepared by Ciampolini[56] using methylated tren and dien ligands. A five co-ordinate intermediate could be favoured if the solvent were a poorly bonding species[2c]. Also, if a negatively charged complex were involved, solvent molecules in the outer sphere might not be oriented correctly for interchange and outer sphere rearrangement could be necessary[44]. The above lines of evidence augur that the existence of $Cr(H_2O)_5^{3+}$ is unlikely. However, a stable five co-ordinate complex of Cr(III), $CrCl_3(NMe_3)_2$, has been prepared by Fowles and Green[57], so the investigation of the penta-aquo intermediate was thought to be worthwhile.
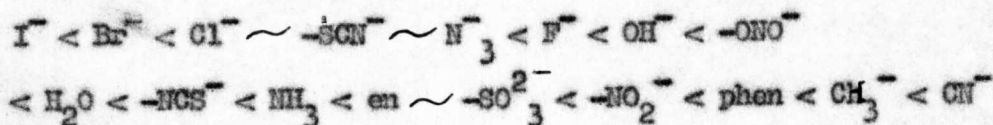
The general associative nature of substitution reactions of the inert Pt(II) complexes has been well documented[1e, 2d], and pentaco-ordinate intermediates or transition states are envisaged. The nature of the entering group is of similar importance to that of the leaving group, and the nature of the trans non-labile ligand also has a profound effect on reaction rates. The kinetic trans effect has been ascribed to the ability of the trans ligand in stabilising the five co-ordinate intermediate or transition state[1e, 2d]. Pt(II), a soft acid, forms more stable complexes with soft bases, by Pearson's hard and soft acids and bases theory (HSAB)[58,59]. A comparison of a list of soft bases[59a] and the order of trans effect ligands[2d] shows a definite tendency for such bases to be high in the trans effect series. It would thus be not unreasonable to predict that stable five co-ordinate complexes of Pt(II) should exist, and several have indeed been isolated[55]. Of particular interest is the trigonal-bipyramidal species $Pt(SnCl_3)_5^{3-}$ [60], since only monodentate ligands are present in the complex. The comparative failure of ligands in octahedral complexes to show trans effects has been discussed by Langford and Stengle[42]. Examples have been reported, however, such as $-SO_3^{2-}$ in trans-$Co(NH_3)_4 X SO_3^{n+}$ (where $X = NH_3$, OH^-, SCN^-, $-NO_2^-$; n = 1 or 0)[46], I^- in $Cr(H_2O)_5 I^{2+}$ [61], and a number of ligands in Rh(III) complexes[62].

The absorptions of energy in the visible region of the electromagnetic spectrum which characterise transition metal complexes are caused by electronic transitions between metal ion d orbitals of different energy. Such absorptions are weak, since the transitions are Laporte, and sometimes even spin, forbidden, and are broad because of coupling with vibrational levels, the non-symmetric modes of which cause the slight breakdown of the selection rules. Photometry has been extensively used in this study for following the reactions of transition metal complexes. This method possesses the major advantage of being non-interfering (in the absence of photocatalysis), and the possibility of the elimination of conflicting reactions by a suitable

choice of monitoring wavelength is also useful. The opportunity of being able to scan spectra during a reaction confers the following additional benefits:

(a) It is often possible to identify products and even intermediates.

(b) The presence of isosbestic points indicates the "cleanness" of a reaction.

A measure of the crystal field splitting parameter, $\triangle$ (the energy difference between the t_{2g} and e_g levels in an octahedral structure), for a certain complex can be deduced from its visible spectrum if corrections are applied for the change in average interelectronic repulsion caused by the transition[1g]. $\triangle$ Values observed for different ligands bound to a typical metal ion increase in the following order:

$$I^- < Br^- < Cl^- \sim -SCN^- \sim N_3^- < F^- < OH^- < -ONO^-$$
$$< H_2O < -NCS^- < NH_3 < en \sim -SO_3^{2-} < -NO_2^- < phen < CH_3^- < CN^-$$

This is an example of a spectrochemical series. The placings above are not identical for every metal ion, though the order is usually very similar. A different position in the above series to that generally accepted has been found in this study for the O-bonded nitrito-ligand when bound to Cr(III). This anomaly will be discussed later.

1-2 Techniques for the Study of Rapid Reactions in Solution

The spate of rate data published on labile systems during the last decade has been due primarily to the development of the necessary rapid reaction techniques. Conventional methods, such as the classical technique of sampling, quenching and analysing, and the manual uses of photometry, electrometry, and polarimetry, still have their place, however, for the study of inert systems. Rapid reactions can occasionally be rendered suitable for study by conventional means by cooling to low temperatures or by the use of very low reagent concentrations.

Rapid reaction techniques have been excellently reviewed[63-8]. The various methods fall into two general categories:

(a) Those in which mixing of reagents is involved.

(b) Those utilising a static sample.

Due to the dead-time between mixing reagents and being able to observe the reaction, the mixing techniques are limited to processes with half-lives of approximately $\geq \frac{1}{2}$ ms. The techniques using a static sample have no such limitation and half-lives down to nanosecond values can be measured.

Relaxation methods, pioneered by Eigen and his co-workers[65a], involve the perturbation of a chemical system in equilibrium, and the observation of the subsequent re-equilibration. The disturbance may be applied in the form of a single pulse, as in the case of the temperature-, pressure-, and electric field-, jump methods, or periodically, by means of ultrasonic waves or a high frequency alternating electric field. Providing that the impulse does not greatly disturb the equilibrium, the relaxation process is first order, irrespective of the molecularity of the reaction, and can be related to the rates of the forward and reverse reactions[28b, 66a].

Relaxation methods have proved especially useful in the study of the formation and dissociation of labile complexes, the temperature-jump technique employing photometric readout having, perhaps, the widest application. The original joule heating apparatus of Eigen[69] is limited to studies of relaxation times of about ≥ 1 μs in conducting solutions. The use of lasers,[70a, 71] and improved modes of joule heating[70b] can extend the time limit well into the nanosecond region, while both laser and microwave[72] heating are applicable to non-conducting solutions.

The ultrasonic perturbation method has been used to detect outer sphere association equilibria occurring in 2:2 electrolyte systems, e.g. the sulphates of divalent metal ions[11, 63a]. ESR has also been used to detect outer sphere association, e.g. with $Cr(H_2O)_6^{3+}$[73]. However, the greatest use of a radiofrequency spectroscopy method in the study of metal

complex reactions has probably been the determination of solvent exchange rates by the NMR line-broadening technique. A recent review[11] presents the theory of the method and the results published to date.

Rapid photolytic and electrochemical methods of studying reaction rates, while extremely useful for many chemical systems, have not found extensive application to metal complexes, though some polarographic investigations have been reported[63b].

Relaxation techniques suffer from the disadvantage of being applicable only to systems possessing viable equilibria. For processes with a large equilibrium constant it is usually impossible to arrange the conditions such that a perturbation will produce a measurable change in the concentrations of the species present. Methods using mixing of reagents do not suffer from this disadvantage. In addition to irreversible reactions, equilibrium relaxation can be studied by means of a mixing technique, using a concentration-jump method[74], for example.

A simple mixing technique is the injection of one reagent into another by means of a hypodermic syringe. However, the mixing efficiency is low, and the author has found that the dead-time is of the order of a few seconds for the addition of one reagent to an equal volume of another situated in a square section spectrophotometry cell. Efficient mixing in a short time interval is best obtained by means of a flow method. The two reagent solutions are forced along separate narrow bore tubes, under turbulent conditions, into a mixing chamber. Observations on the ensuing reaction are made in the exit tube from the mixer. A variety of techniques have been used to detect the progress of the reaction including photometry, conductivity, temperature and pH measurements. Alternatively, the mixed solution may be quenched by addition to a third reagent, or by rapid cooling. No special detection equipment is required for quench flow, since the samples can be analysed at leisure and the extent of reaction at the point of quenching established. Many factors influence the efficiency of flow equipment (e.g. flow rate and the sensitivity of the detection

system), but none is perhaps more critical than the performance of the mixer, into designs of which has gone much effort and ingenuity[64a, 67].

The original apparatus of Hartridge and Roughton[75] was of the continuous-flow type. Using this mode, solutions are driven continuously through the system by gas pressure, while measurements are made at intervals along the length of the exit tube to establish the extent of reaction at different times after mixing. Alternatively, observations are made at one point and several runs are carried out using different flow rates. Dalziel[76] has designed a continuous flow apparatus which employs a standard Beckmann spectrophotometer as the detector. Motor driven syringes, first introduced by Dirken and Mook[77], are now generally used to deliver reagents. Continuous-flow is a comparatively simple technique in that rapid response detection is not required. A dead-time of the order of $\frac{1}{2}$ ms can be easily achieved and the utilisation of very sensitive observation methods permits high accuracy and the use of dilute reagents. Large volumes of reagents must, however, be consumed, which is a grave disadvantage for many chemical systems.

With the advent of rapid response detection methods, other techniques became feasible. Chance's accelerated flow apparatus[78] was developed so that small volumes of reagents could be used. Reagent solutions in small syringes are discharged through the flow system by a sharp manual push. Photometric detection is employed in one position directly after the mixer and the light intensity is displayed as the Y-deflection on an oscilloscope screen. The flow rate varies during the run, but is sensed from the movement of the driving syringe pistons and displayed as the X-deflection on the oscilloscope. The spot is photographed traversing the oscilloscope screen and the trace is analysed to determine the rate of reaction. This method possesses no particular advantage over the simpler stopped flow technique, which has largely superseded it.

The stopped-flow technique (SF) has quickly developed into perhaps the

most popular fast reaction research tool, and has been extensively used in this study. A manual, motor, pneumatic or hydraulic drive forces the reagents out of syringes and rapidly through the flow system. When sufficient volumes (ca. $\frac{1}{2}$ ml. total) of fresh reagent solutions have been delivered to purge the mixer and observation tube the flow is abruptly arrested. The whole course of the reaction can then be observed in a static sample at a point immediately after the mixer. The method was first described by Roughton[79], improved by Chance[80], and finally perfected by Gibson[81].

A multitude of designs [67a,b,80-5] of SF equipment have been described, with dead times of between two and fifteen milliseconds between mixing and the initial detection of the reaction. The time resolution of SF is thus not quite as good as that of continuous flow (CF). A recent design by Berger[86], however, uses very high driving pressures and special valves to arrest the flow. It is claimed that reactions with half-lives of less than $\frac{1}{2}$ ms can be studied using this apparatus. An instrument capable of working at very low temperatures has been described by Caldin[87], and promises to be a useful development of the SF technique. An improved version of Caldin's apparatus, constructed of completely inert materials, is currently being developed in this Department.[88]

Many hybrid designs have been published, incorporating SF with another rapid reaction technique. Examples include the SF/temperature-jump instrument of Erman and Hammes[89], and the flow/flash apparatus of Gibson and Greenwood[90]. Current advances in SF technology include the application of on-line computing[64b, 70c], for the rapid calculation of rate data, and rapid scanning spectrometry, to obtain the spectra of transient intermediates[91].

Flow techniques were developed originally by physiologists and bio-chemists, but their rapid adoption by inorganic chemists during the last fifteen years has resulted in a wealth of rate data on the reactions of metal

complexes which is too vast to catalogue.   The recently instituted
commercial production of various designs of SF equipment by the American
Instrument Co., Inc. and Durrum Instrument Co. cannot but encourage even
greater expansion by making the technique widely available.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1. The Stopped-flow Apparatus

(a) Description

The stopped-flow apparatus used in this study is almost identical to that described by Gibson and Milne[84], though a few detail(ed modifications have been made. The plan and elevation of the design are shown in Figures 4 and 5. As supplied by the University of Sheffield workshops, the flow unit was constructed of stainless steel which was found to be attacked by the high perchloric acid concentrations ($\leq$ 2M) used in some experiments. To avoid contamination of the solutions by dissolved metal ions, the whole flow system between the driving syringes and the Kel-F mixers was rebuilt in inert materials. The stainless steel observation tube, 2 cm long and fitted with quartz windows, was, however, retained due to the difficulty of producing one sufficiently robust and efficiently thermostatted from PTFE. The short time that the mixed solution remains in the observation tube during the reaction is scarcely long enough for significant contamination to occur.

The delivery block (H in Figures 4 and 5) was replaced by one of identical design made from glass-filled PTFE. The new valve block (K in Figures 4 and 5, shown in detail in Figure 6) consists of a glass-filled PTFE core surrounded by a stainless steel box section. The bolts retaining the valves are screwed into the stainless steel, but all solution pathways and valve seats are machined in the PTFE core. The plunger valve design of Gibson[84] was dispensed with, diaphragm valves being used. This type of valve has the following advantages over the plunger valve :
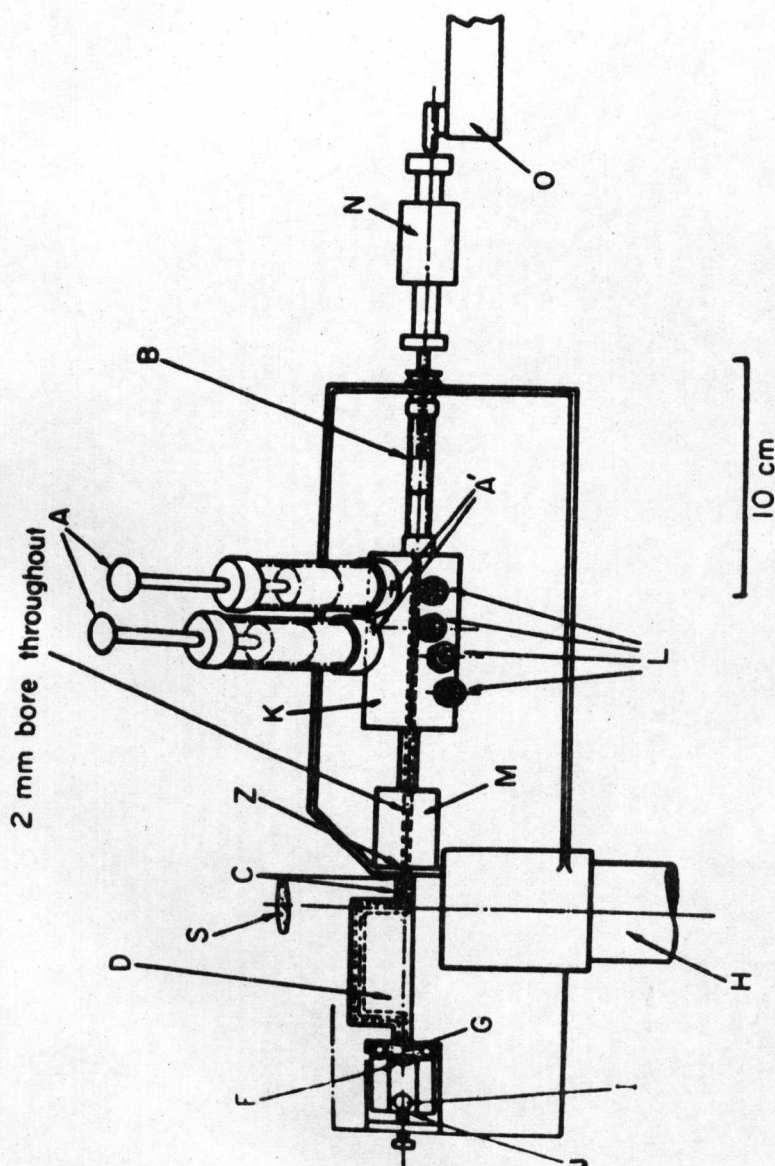
Plan view of flow apparatus. A, Reservoir syringes (25 ml); A', tapered ports for reservoir syringes (1-in-10 record taper); B, driving syringe (2 ml); C, two mixers; D, observation chamber; F, stop syringe (2 ml); G, stop; H, photomultiplier housing; I, port valve; J, drain port; K, valve block (stainless steel); L, valves; M, delivery block (stainless steel); N, syringe-pushing block; O, Armstrong R.C. 8 hydraulic actuator; S, biconvex quartz lens (25 mm diameter × 50 mm focal length); Z, baffle. The crosses on the valve block (K) show the positions of the valves (L) and of the tapered ports (A') for the reservoir syringes (A).

FIGURE 4

FIGURE 5
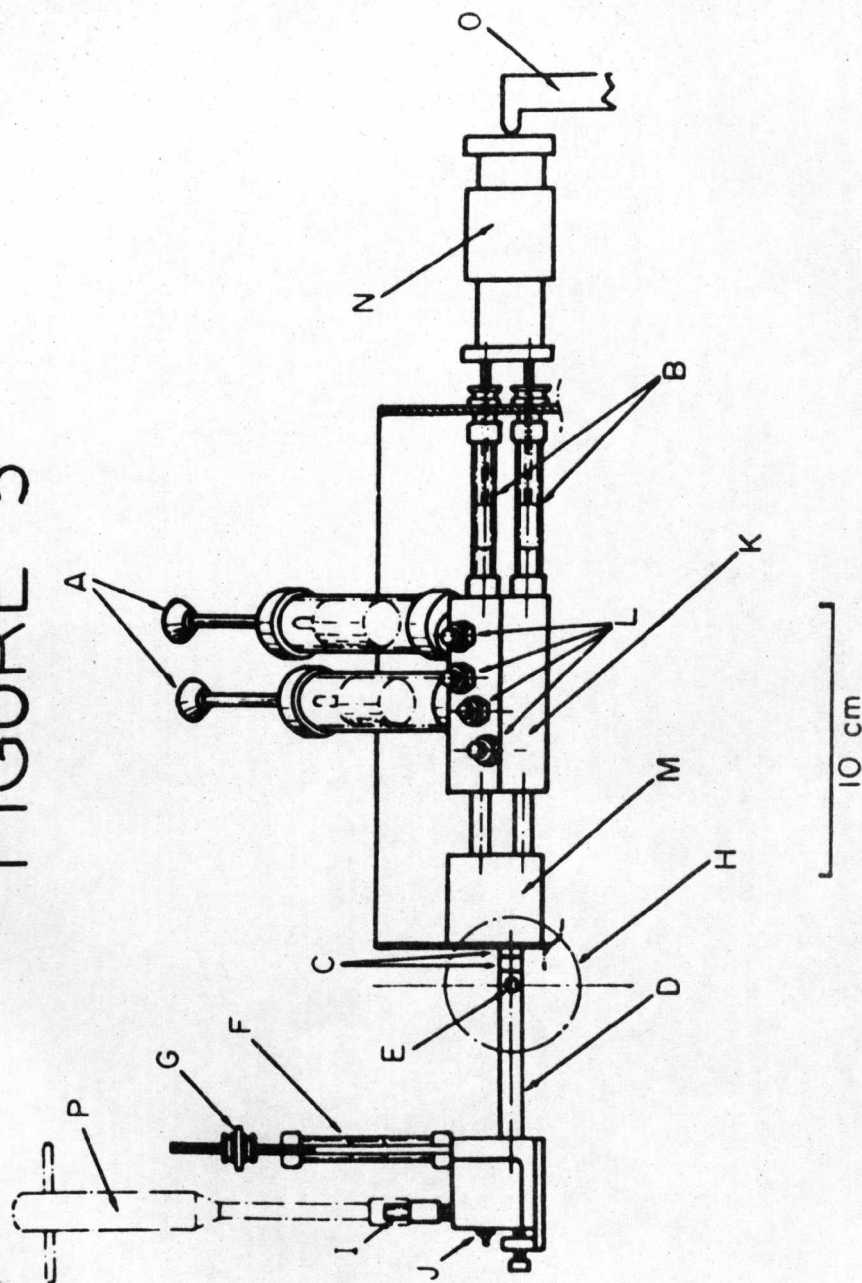
Side elevation of flow apparatus. *A*, Reservoir syringes (25 ml); *B*, driving syringes (2 ml); *C*, two mixers; *D*, observation chamber; *E*, observation window; *F*, stop syringe (2 ml); *G*, stop; *H*, position of photomultiplier; *I*, port valve; *J*, drain port; *K*, valve block; *L*, valves; *M*, delivery block; *N*, syringe-pushing block; *O*, lever to Armstrong R.C. 8 hydraulic actuator; *P*, position of key for operating stop valve.

SECTION C-C

SECTION A-A

SCALE:

1"

STAINLESS STEEL

GLASS FILLED P. T. F. E.

O·5mm P. T. F. E. SHEET

SECTION B-B
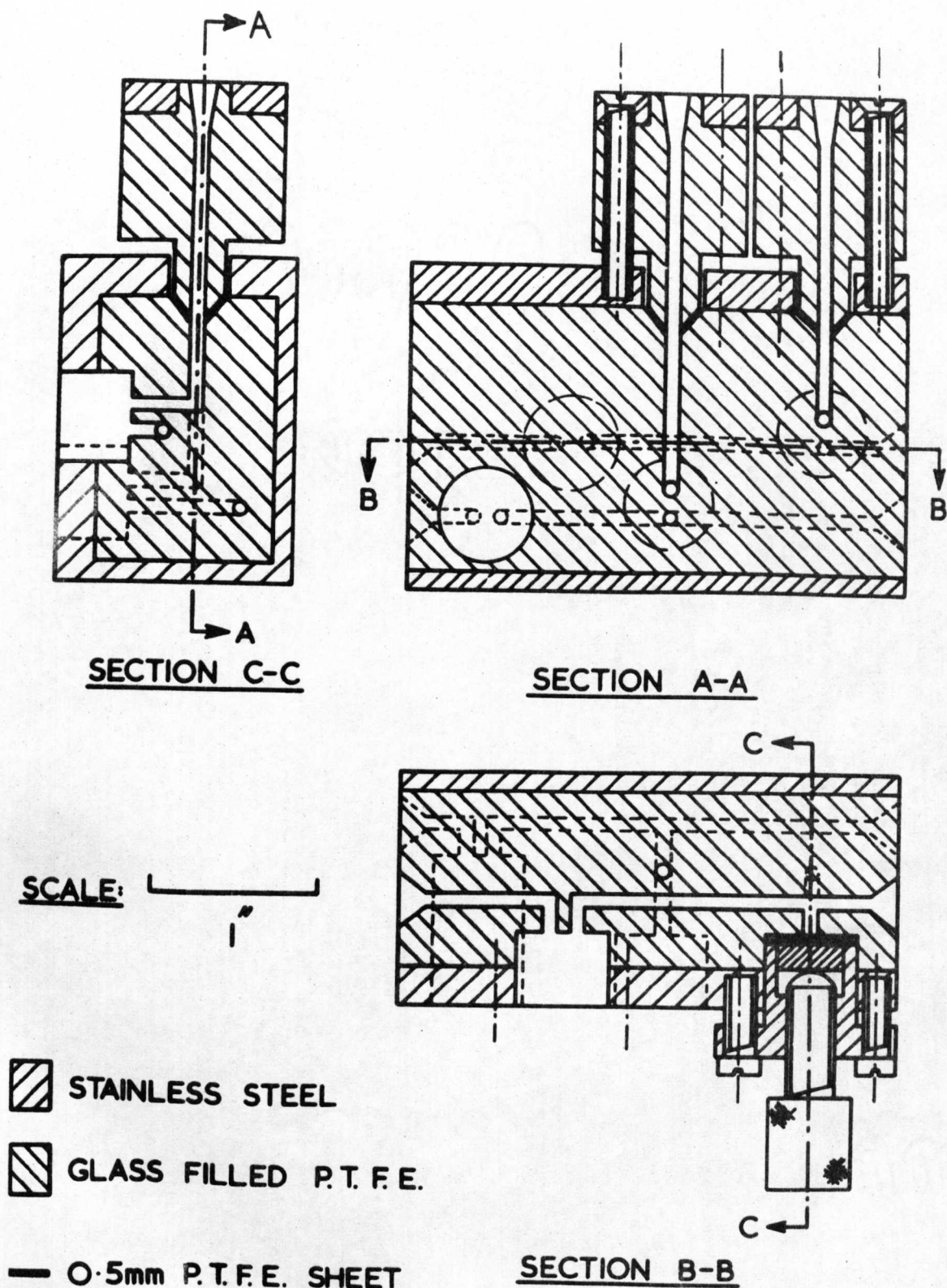
DIAPHRAGM VALVE BLOCK

FIGURE 6

(a) There is no initial resistance to flow.

(b) The solution displacement volume is very low.

(c) The possibility of solution leakage into the body of the
     valve is reduced.

"Bounce" of the diaphragms on stopping the flow does not appear to be
a problem if sufficiently thick (ca. 0.5 mm) PTFE sheet is used.   The
stainless steel bodies of the valves are regularly lubricated with
silicone grease to promote smooth operation and inhibit corrosion by
preventing the ingress of thermostatting water.   The valve diaphragms
need to be replaced only very rarely.   Driving syringes are of the 2 ml
Everett "Record" type with PTFE tips replacing the original metal fittings
(Figure 7).   Glass pistons are used, consisting of the seam-off end
section from an Everett 2 ml all-glass syringe into which a stainless
steel shaft is "potted" with silicone rubber (Figure 7).

To minimise vibration the flow unit is mounted on a heavy steel
plate fitted with four levelling screws.   To the side of this plate
an optical bench is firmly attached on which are mounted the light source
and monochromator.   The signal from the photomultiplier is taken to the
oscilloscope via an emitter-follower circuit (Figure 9), constructed by
the author.   I am indebted to Dr.J.P.Candlin and the Electronics
Department, Petrochemical and Polymer Laboratory, I.C.I. Ltd., Runcorn
for this design.   The anode current of the photomultiplier is monitored
using this circuit, and high frequency noise can be attenuated using an
R/C filter.   The circuit also generates an adjustable "backing-off"
voltage which is applied to the second input of the oscilloscope
differential amplifier.

Peripheral equipment used with the stopped-flow unit is listed below :

Oscilloscope   Tektronix storage 'scope, type 564, with 2A63
differential amplifier and 2B67 timebase.

Photomultiplier   E.M.I. type 9529B (quartz end window).   All
dynodes are utilised, connected by 100K resistors.

FIGURE 7

DRIVING SYRINGE & METHOD OF LOCATION

valve block

thermostat bath wall

hexagon head

knurled ring

Actual Size

KEY

p.t.f.e.

glass

stainless steel

silicone rubber

● — O-ring
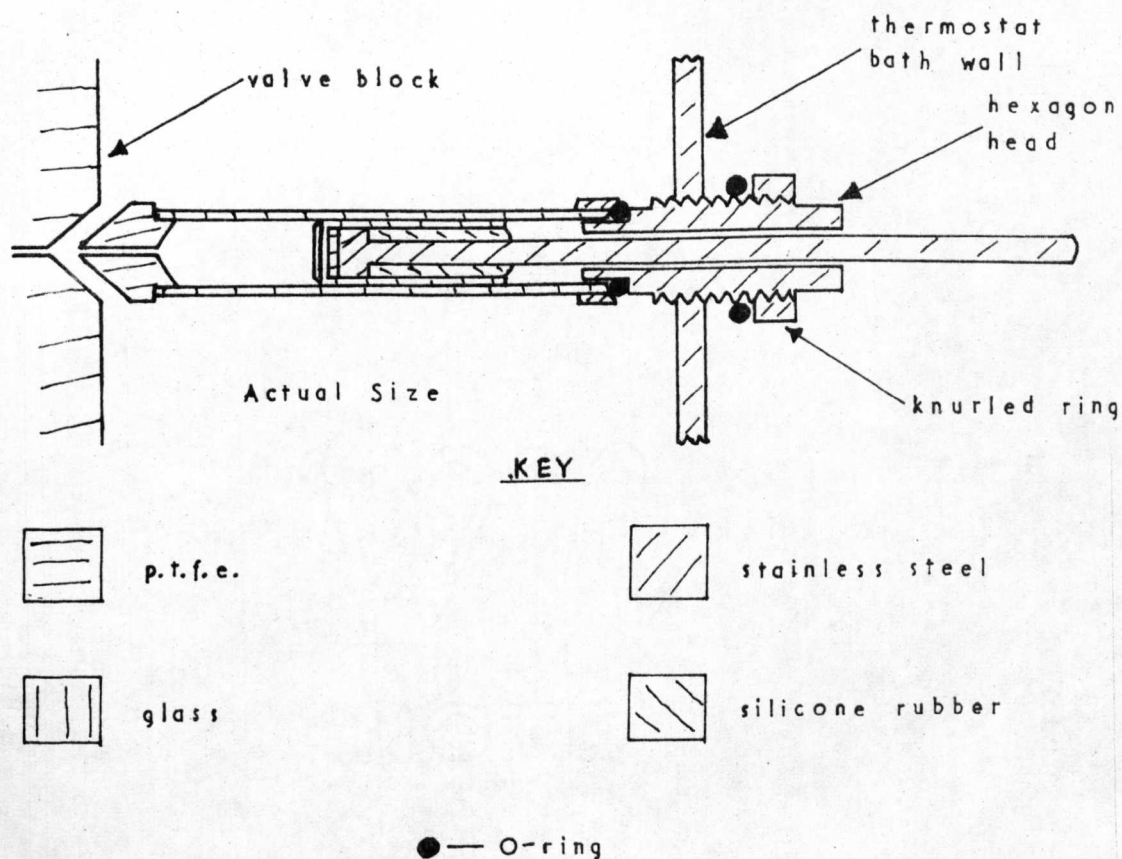
FIGURE 8

OSCILLOSCOPE TRIGGER CIRCUIT

microswitch

$1 M\Omega$

oscilloscope

47Ω

$0.5\mu f$

$4.5 V$

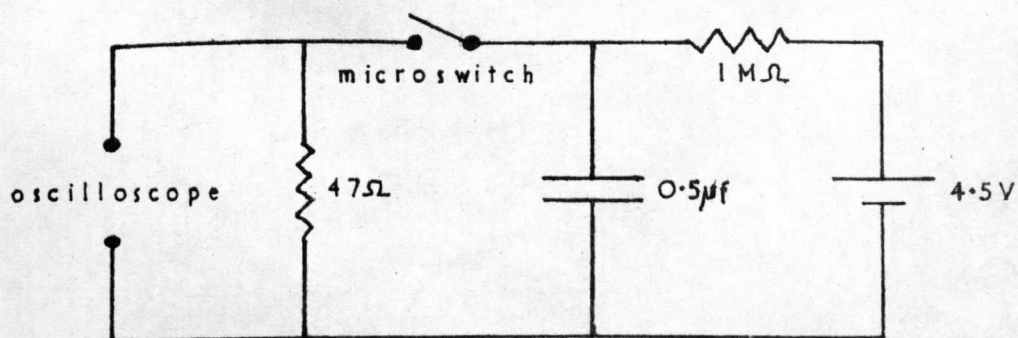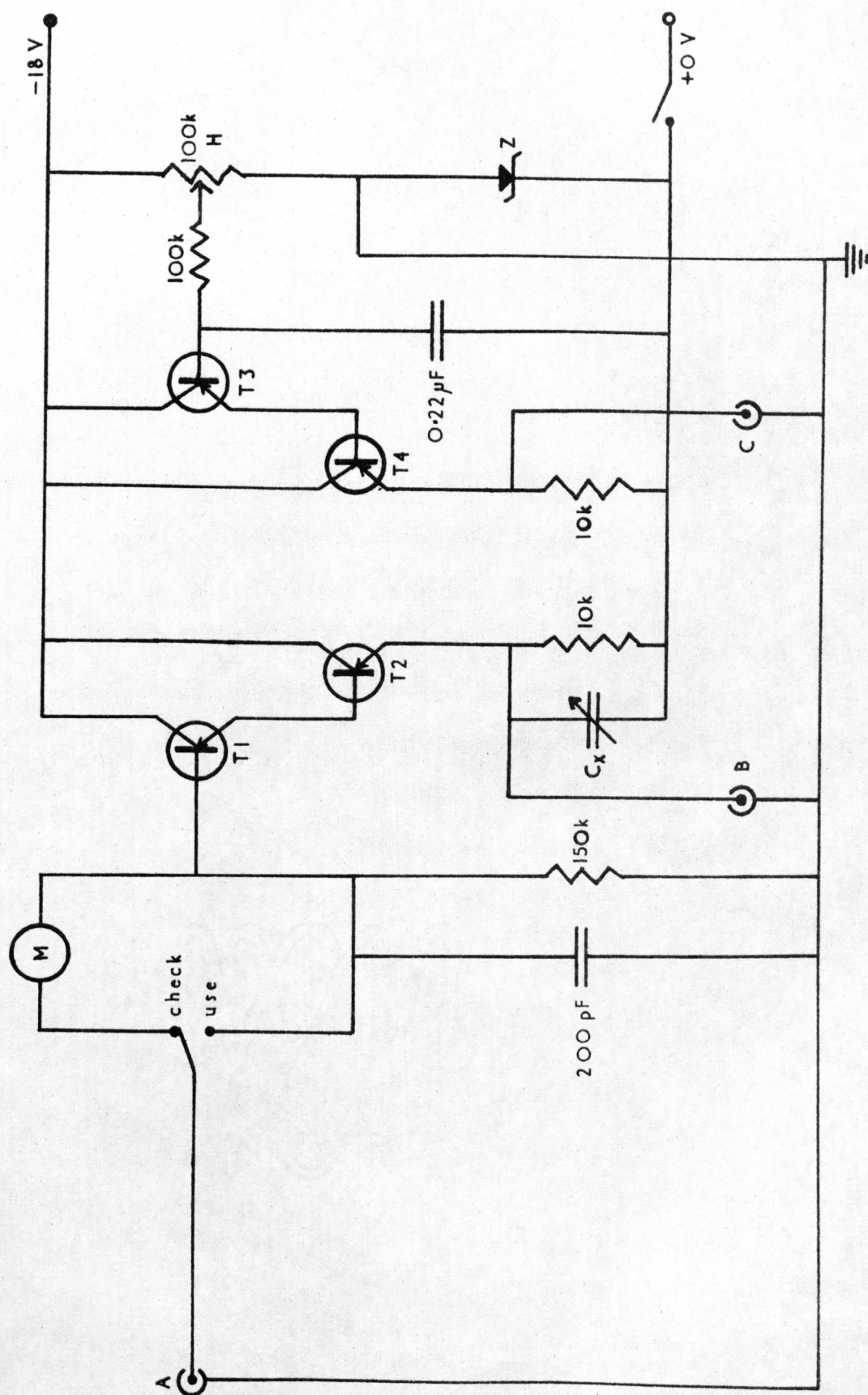## FIGURE 9

Emitter-follower circuit used with stopped-flow instrument.

A   Input from anode of photomultiplier.

B   Signal output to oscilloscope.

C   "Backing-off" voltage output to oscilloscope.

C_x Switched bank of capacitors, 0.1 – 100µF.

H   Ten-turn helipot.

M   0 – 25 µA meter.

T   1 – 4, type BCZ 11.

Z   3.3V zener diode.

Photomultiplier Power Supply   Fluke type 412B (0 - 2.1 KV).

Monochromator   Bausch and Lomb fitted with wide range, high intensity grating (180 - 700 nm, Catalogue No. 33-86-07) and adjustable slits.

Light Sources   U.V. - Bausch and Lomb 45W deuterium lamp. Visible - Osram 200W quartz-iodine lamp.

Light Source Power Supplies   U.V. lamp - 0.6A constant current stabilised, built by the author to the design of Grenson Electronics Ltd.   Visible lamp - 8A constant current stabilised, built by the author from a module supplied by Grenson Electronics Ltd..

Oscilloscope Trigger   External, by means of a microswitch fitted to the stopping-block (G in Figures 4 and 5).   A simple circuit designed to prevent spurious triggering when the microswitch "breaks" is shown in Figure 8.

Oscilloscope Camera   Telford type A, using Polaroid 46-L transparency film.

Syringe Drive   Armstrong hydraulic, master unit decoupled to reduce vibration.

Thermostat   External bath.   A pump circulates thermostatting water around the flow unit.   Temperature range 273 - 323 K.   Stability ± 0.1 K.   Flushing of the light path with dried air is employed for temperatures below the dew point.

(b)   **Performance and Operation**

The optical and electronic performance of the instrument should be very similar to that of the commercial Durrum spectrophotometer.   The mechanical and hydraulic performance appears to be unchanged from that of the original design[84].   First-order rates of up to 150 s^{-1} have been successfully measured.   A typical set of oscilloscope traces and the corresponding rate plots are illustrated in Figure 10, which shows the excellent reproducibility attainable.   The machine was checked for 1 : 1

FIGURE 10

Upper — photograph of oscilloscope screen

showing four consecutive kinetic runs.

Sensitivity 0.1V/division. timebase 20 ms/division.

Lower — computer plotter output

showing the rate plots of the above runs.

Computer program R026/01 (Appendix 2).

The reaction portrayed is :

$$Cr(H_2O)_5N_3^{2+} + HNO_2 + H^+ \longrightarrow Cr(H_2O)_6^{3+} + N_2O + N_2$$
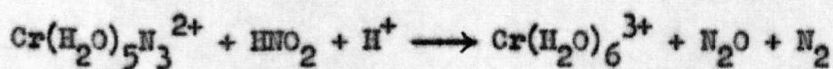
$[Complex]$ ca. 5×10^{-5}M $\qquad\qquad [H^+] = 0.50$M

$[HNO_2] = 0.01$M $\qquad\qquad [Cl^-] = 0.02$M

$I = 1.0$ (NaClO$_4$) $\qquad\qquad$ Temperature $= 298.1$ K

$\lambda = 272$ nm $\qquad$ Monochromator exit slit $= 0.4$ mm

Photomultiplier voltage $= 568$V $\quad$ Filter time constant $= 1$ ms.
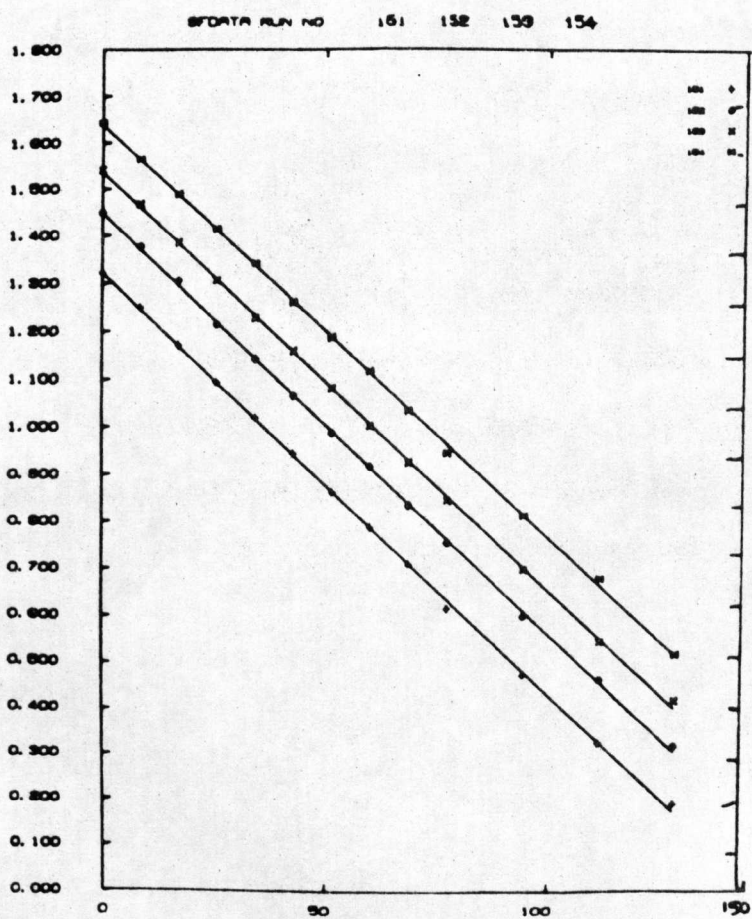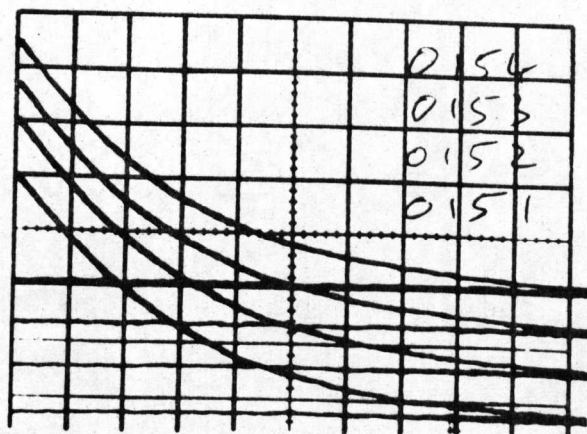
mixing and found to be satisfactory.   Outgassed solutions were not required in the kinetic determinations reported in this dissertation, probably because all SF runs were carried out at, or below, ambient temperature.   No evidence of cavitation was observed.   The two reagent solutions were prepared with equal ionic strength whenever possible. Since it was found possible always to use transparent solutions giving a large change in transmittance on reaction, noise on oscilloscope traces was never a problem, and reaction rates could be calculated with precision ($\pm$ 1%).   A low range of photomultiplier anode current was employed to ensure linearity (0 - 10 μA = 0 - 100% transmittance). Monochromator exit slits of 0.4 - 1.0 mm and photomultiplier voltages in the range 500 - 700 V were found to be convenient.   When using the R/C filter to reduce noise on traces, care was taken that the time-constant applied did not exceed 5% of the half-life of the reaction being measured, to ensure that no distortion of the traces occurred[84]. To avoid the risk of obtaining erroneous rates due to machine trouble or following a side reaction, optical density changes were calculated for every run.   The changes were compared with those expected from the known extinction coefficients of reactants and products, and any runs for which the changes did not tally were rejected.   The amplifier sensitivity and timebase of the oscilloscope were calibrated using the internal standard.

(c)   Calculation of Results

Two to four runs under the same reaction conditions were recorded on the oscilloscope screen, with a small vertical displacement between each one (Figure 10).   The screen was photographed and the resulting transparency projected by means of a photographic enlarger.   The reaction curves were traced onto graph paper and reduced to sets of (x,y) co-ordinates by manual measurements.   The sets of co-ordinates together with factors to convert x to time, and y to transmittance

values were analysed by computer using program RO26/01 (Appendix 2).
The computer program carries out the following operations :

(a) Conversion of transmittance to absorbance values.

(b) Linear least-squares determination of the best straight line
fit to a plot of $\ln(D_t - D_{inf})$ versus t (where D_t and D_{inf}
are the absorbances calculated for times t and infinity,
respectively). For a first-order reaction

$$\ln(D_t - D_{inf}) = -kt + c$$

(c) Print-out of the rate constant, k, with its associated error.

(d) Presentation of the rate plot derived above by means of a
digital plotter accessory (see Figure 10 for an example of
this output).

The rate plot of every run was examined since it was found by experience
that quite marked curvature could be exhibited with little effect on the
magnitude of the calculated error. The results of any runs showing
curved rate plots were rejected.

2.2. Spectra

(a) U.V. and Visible Regions (200 - 700 nm).

Stoppered "Spectrosil" square section 1cm pathlength, or cylindrical
2, 5, and 10cm pathlength cells were used as appropriate. A Cary 14
recording spectrophotometer was employed for all spectra, which were
determined in aqueous solution at room temperature against a water blank,
unless specified otherwise. The sample and reference compartments of
the Cary 14 could be thermostatted in the range 273 - 323 K. At
temperatures below the dew point the optical pathways of the instrument
were purged with pure, dry nitrogen.

(b) I.R. Region (4000 - 250 cm^{-1})

A Perkin-Elmer 457 recording infra-red spectrophotometer was used.
Spectra were recorded with samples in the form of KBr discs, except on
a few occasions when Nujol mulls between CsI plates were employed.

2.3. Photometric Determination of Kinetics.

Photometric kinetic determinations were performed using one of four techniques, depending on the half-life ($t_{\frac{1}{2}}$) of the reaction studied :

1. $t_{\frac{1}{2}} < 1$ minute. The stopped-flow method at fixed wavelength was used, as described above.

2. $1 < t_{\frac{1}{2}} < 30$ minutes. The Cary 14 spectrophotometer was utilised. The reaction was initiated by the addition to a prethermostatted solution in a cell situated inside the instrument of, either a small solid sample by means of a glass paddle, or another solution from a syringe. A thermostatted Jencons "Repette" syringe was employed to add the reagent solution, and usually a volume of 1.6 ml was injected into an equal volume in a 1 cm pathlength cell. The syringe was fitted with a specially-made PTFE needle, which passed through the lid of the sample compartment of the spectrophotometer, right down into the cell, but keeping well clear of the light beam. Using this device, accurate 1 : 1 mixing could not be relied on, so solutions were analysed after the reactions were complete (e.g. for $[H^+]$). However, both reagent solutions were prepared having the same ionic strength (i.e. 1.0), so errors in this parameter were eliminated.

Reaction rates in this time range were usually obtained at fixed wavelength. Measurements were made continuously using the length of the chart paper as the time scale. When the reaction appeared to be nearly over (> 90% complete), the cell was withdrawn from the light beam, and the absorbance then checked only occasionally until there was no further change, when the final reading was recorded.

3. $30 < t_{\frac{1}{2}} < 200$ minutes. The Cary 14 spectrophotometer was again employed. However, solutions were now prepared remote

from the instrument, added to a cell and allowed to thermostat inside the sample compartment for ca. 15 minutes before commencing observations. Spectra were scanned at measured time intervals, the sample being removed from the light beam in the intervening periods in order to reduce photolysis, which is known[li] to occur to a slight extent with Cr(III) complexes, to a minimum. Reactions were followed until there was no further change, or until spectra failed to intersect the original isosbestic points.

4. $t_{\frac{1}{2}}$ > 200 minutes. Reactions were followed at fixed wavelength using a Gilford "2000" Multiple Sample Absorbance Recorder fitted to a Zeiss M4 QII monochromator. The sample compartment of the instrument can be thermostatted in the range 293 - 323 K. The sample changer holds four 1cm pathlength cells, and was programmed to record the absorbance of each every 15 minutes. Since the instrument operates in single beam mode and observations were carried out for long periods (up to three days), a blank cell was always included during kinetic runs so that the effect of drift could be allowed for. In the interim periods between readings it was arranged that the blank cell occupied the position in the light beam. Hence the reacting samples were exposed to light only for a few seconds every 15 minutes.

The above techniques were not adhered to rigidly in the time ranges quoted. Indeed, some deliberate overlap was introduced to ensure that reaction rates were not affected by different modes of measurement. In no case were discrepancies observed greater than the limits of experimental error.

All kinetic experiments in this work were carried out at a constant ionic strength of 1.0 using added sodium perchlorate, except where otherwise indicated. Pseudo first-order conditions were employed. First-

order rate constants from conventional photometric measurements were
calculated using computer program R001/02 (Appendix 2), which performed
an unweighted linear least-squares best fit to a plot of values of
$\ln(D_t - D_{inf})$ versus time. In circumstances where it was impossible
to obtain a valid absorbance reading at infinite time (e.g. because of
a subsequent reaction), a value was estimated using the method of
Swinbourne[96]. Computer program R001/08 (Appendix 2) was used for this
purpose.

2.4. Activation Parameters

Computer program R002/06 (Appendix 2) was used for the calculations.
The Arrhenius factors, E_a (activation energy) and A (frequency factor)
from the relation $k = A \exp(-E_a/RT)$ were calculated from a linear
least-squares best fit line to a plot of weighted values of ln k versus
$1/T$. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the transition-state theory
equation, $k = KT/h.\exp(\Delta S^{\ddagger}/R).\exp(-\Delta H^{\ddagger}/RT)$, were derived for 298.1 K
by means of the relations :

$$\Delta H^{\ddagger} = E_a - RT$$
$$\Delta S^{\ddagger} = R(\ln A - \ln(KT/h) - 1)$$

These equations apply for both uni- and bimolecular reactions in solution[28c].

2.5. Treatment for Error

All errors quoted in this work are of one standard deviation. Data
(where appropriate) was weighted by the reciprocal of the square of its
associated error. The formulae used in calculations and computer
programs are to be found in Beers' monograph[97].

2.6. Preparation of Stock Solutions

(a) Sodium Nitrite, Nitrate, and Chloride

$NaNO_2$, $NaNO_3$, and NaCl standard solutions were prepared by weight
from dried A.R. materials.

(b)   Sodium Thiocyanate

Recrystallised G.P.R. material was used.   A solution of approximately the required concentration was prepared, then standardised argentimetrically by a volumetric method employing an absorption indicator[92].

(c)   Sodium Perchlorate

Standard sodium perchlorate solution was prepared by carefully neutralising a solution of A.R. sodium carbonate with A.R. perchloric acid (60%).   Samples were analysed by evaporating aliquots at ca. 390 K and weighing the solid $NaClO_4$ residue.

(d)   Perchloric Acid

Diluted A.R. perchloric acid (60%) was standardised by titration with 1N NaOH "Volucon" reagent.

2.7.   Analyses

(a)   Nitrogen and Halogens

Solid samples were assayed by a commercial analytical service.

(b)   Chromium

Chromium was estimated photometrically as chromate ion (E_M = 4830 at 372 nm), after alkaline oxidation with hydrogen peroxide.   A Pye-Unicam SP500 spectrophotometer was used for determining absorbance readings.

(c)   Sulphate Ion

SO_4^{2-} was analysed gravimetrically as $BaSO_4$.

(d)   Nitrite Ion

Two methods were used :

(i)   An iodometric technique was employed in the earlier parts of this work.   The method was that of Rao and Pandalai[93], as modified by Fee et al[94].

(ii)   A photometric method was later found to be more accurate and

convenient. This involved the diazotisation of sulphanilamide and coupling with N-(1-naphthyl)ethylenediamine[95]. Two solutions were prepared :

    <u>A</u>.   1.0g sulphanilamide in 100 ml 20% HCl.

    <u>B</u>.   20mg N-(1-naphthyl)ethylenediamine hydrochloride in 100 ml water (stored in a darkened flask).

To a few ml of nitrite sample (containing <u>ca</u>. 10^{-7} mol) were added 2 ml of solution A, 1 ml conc. HCl, and 2 ml of solution B, and the volume of the whole made up accurately to 10 ml. The colour was allowed to develop for 20 - 40 minutes in the dark, and the absorbance of the solution determined in a 1 cm pathlength cell at 540 nm, using an SP 500 spectrophotometer. The nitrite concentration in the 10 ml test sample was ascertained from a calibration graph (Figure 11).

(e)   <u>Chloride Ion in Solution</u>

Chloride ion concentrations were determined potentiometrically using a solid-state chloride ion selective electrode (Orion type 96-17). The electrode contains its own reference and was coupled to a Radiometer model 4 pH meter, used on its millivolt range. A plot of potential versus $\log[Cl^-]$ was found to be linear in the concentration range 2×10^{-3}M to 10^{-1}M, with the slope of the line solely defined by the temperature of the measured solution. However, the position of the line with respect to the potential axis alters with the concentration and nature of the other species in solution (Figure 12). Thus the electrode was always calibrated using solutions with the same background composition and temperature as the unknown.

FIGURE 11

Calibration graph for the estimation
of nitrite ion by the photometric method.
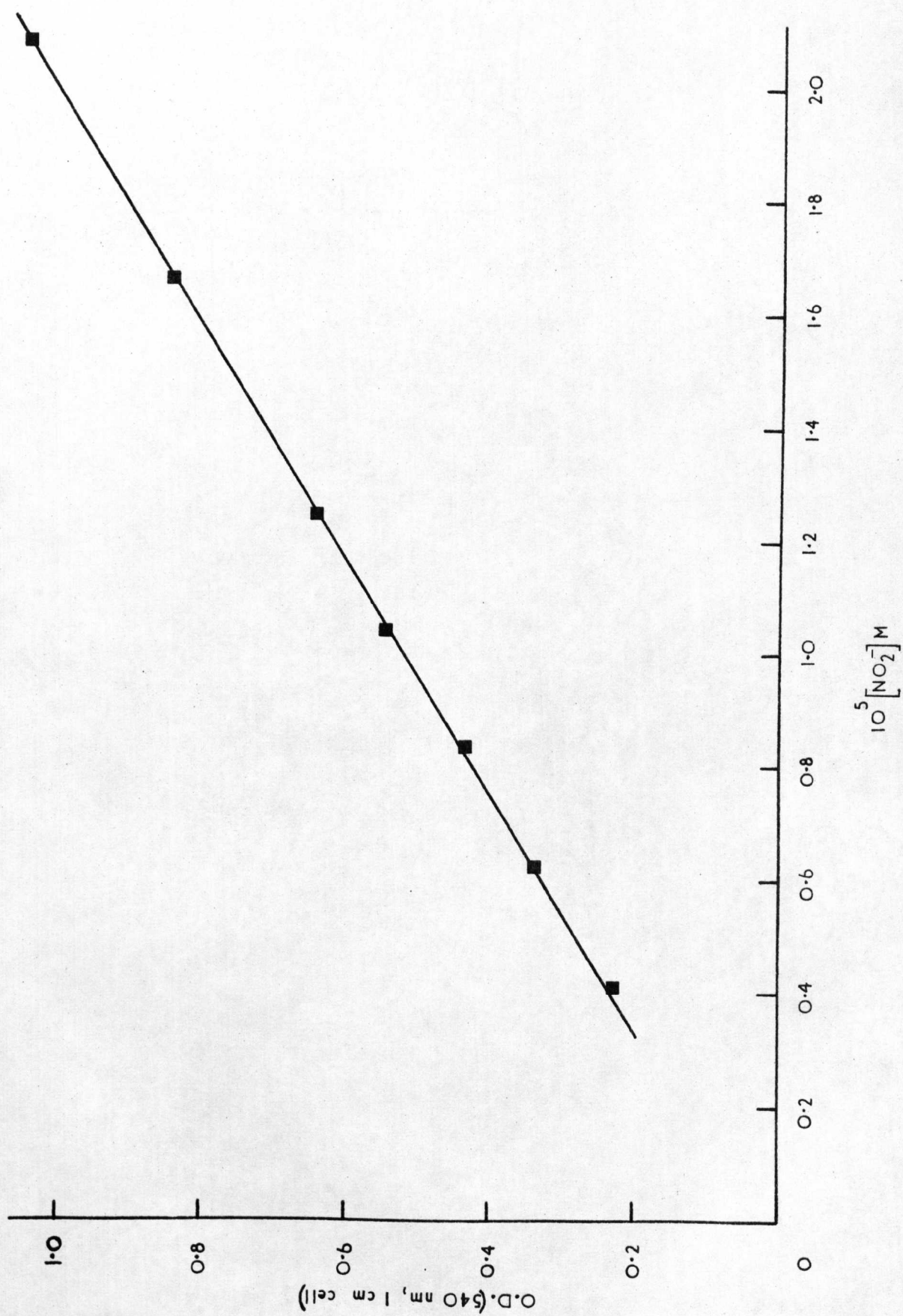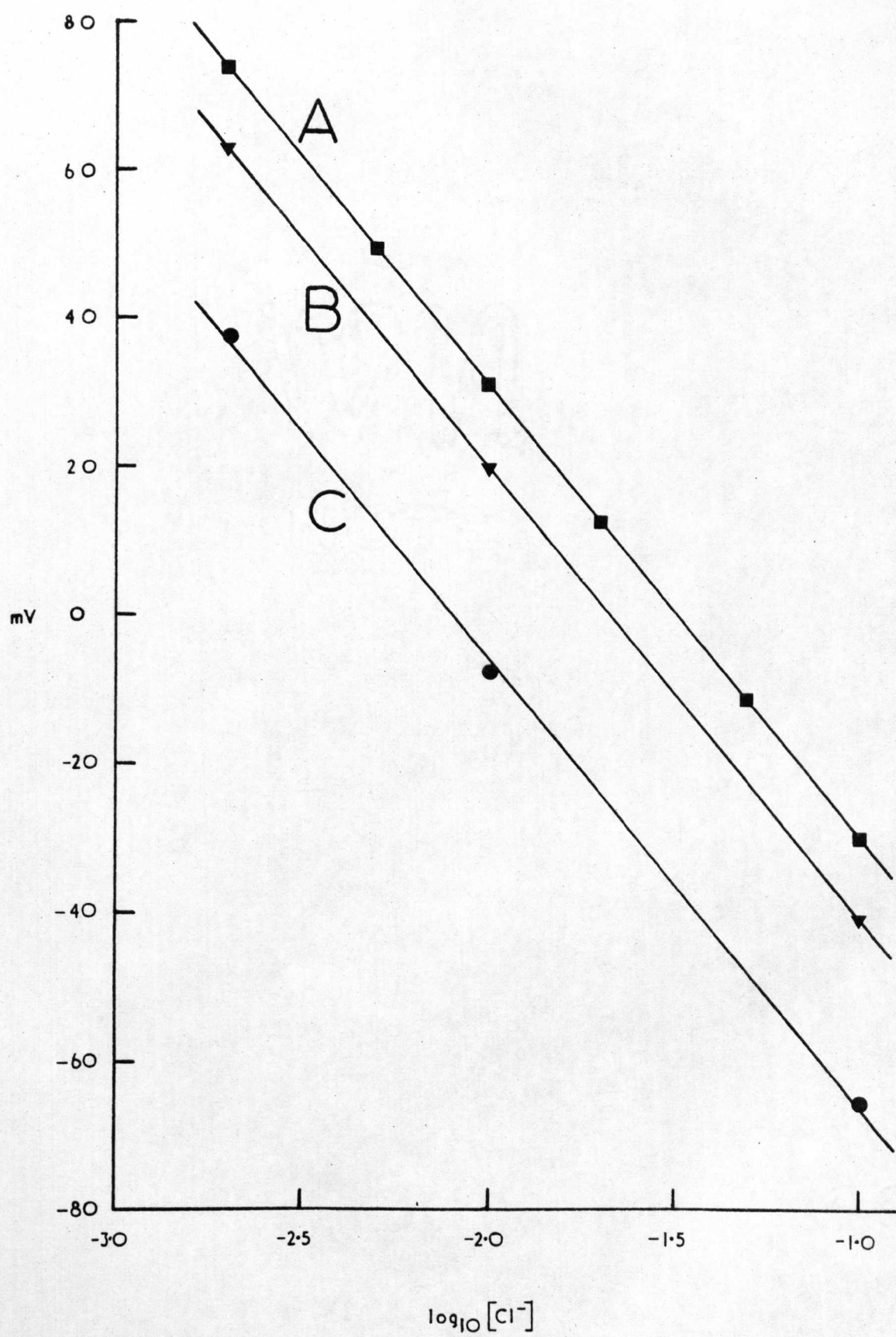
O.D. (540 nm, 1 cm cell)

$10^5 [NO_2^-] M$

FIGURE 12

Calibration plots for the Orion

chloride ion selective electrode

(Model 96-17) at 308.1 K.

A $I = 1.0$ ($NaClO_4$)

B $[HClO_4] = 0.1M$, $[HNO_2] = 0.04M$,

             $I = 1.0$ ($NaClO_4$)

C $I = 1.0$ ($HClO_4$)

CHAPTER 3

THE NITROUS ACID OXIDATION OF THE
AZIDOPENTA-AQUOCHROMIUM(III) ION,
AND COMPETITION EXPERIMENTS DESIGNED
TO DETECT A FIVE CO-ORDINATE INTERMEDIATE

3.1. Introduction

Competition methods for detecting intermediates of reduced co-
ordination number in the reactions of octahedral complexes have been
extensively applied in recent years, chiefly to penta-ammine complexes
of cobalt(III).   The generation of an intermediate has been sought in
both spontaneous and induced dissociations of ligands.   As outlined in
Chapter 1, for detection a five co-ordinate intermediate must exist long
enough to be discriminating in its subsequent reaction.   Thus, if two
species, Y and Z, are present when an intermediate is generated with
which they are able to react, the following competition ensues :

$$ML_5 + Y \xrightarrow{\quad k_y \quad} ML_5Y$$

$$ML_5 + Z \xrightarrow{\quad k_z \quad} ML_5Z$$
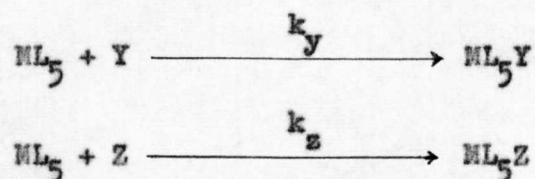
A discrimination, or fractionation, factor can be defined as
$F = [ML_5Y][Z]/[ML_5Z][Y]$, where $[ML_5Y]$ and $[ML_5Z]$ are the final
concentrations obtained, and $[X]$ and $[Y]$ are both in large excess over
$[ML_5]$.   In kinetic experiments, as described in Chapter 1, $F = k_y/k_z$.
A constant discrimination, or fractionation, factor should be obtained
for a wide range of leaving groups and methods of generation, for the
existence of a common intermediate to be indicated in a particular set
of reactions.   In this chapter, "discrimination" will be used when Y
is an entering anion and Z is solvent, while "fractionation" will mean
competition between two isotopically or chemically different solvents.
X will represent a leaving group and L a non-reacting ligand.

Posey and Taube[98] compared the $H_2^{16}O/H_2^{18}O$ proportion in bulk solvent with that obtained in the products of the induced aquation reactions of $Co(NH_3)_5X^{2+}$ ($X^- = Cl^-$, Br^-, I^-) reacting with Ag^+, Hg^{2+}, and Tl^{3+}. Using Hg^{2+} a constant fractionation factor favouring $H_2^{16}O$ incorporation was found for all three complexes, and the authors postulated that an intermediate was indeed formed in this case. Results using Ag^+ and Tl^{3+} were more variable, and it was proposed that a concerted process occurred with the electrophile placing a water molecule from its outer-sphere on the cobalt atom as it removed X^-. Competition experiments with SO_4^{2-} and NO_3^- were also reported, the results of which tended to support the existence of an intermediate, though the work with sulphate was complicated by ion-pair formation, not only with the cobalt complex, but also with the attacking metal ion.

Haim and Taube[99] attempted the generation of $Co(NH_3)_5^{3+}$ by means of the nitrous acid oxidation of the co-ordinated azido group in $Co(NH_3)_5N_3^{2+}$. The transient species $Co(NH_3)_5N_4O^{3+}$ was thought to be the initial product which could rapidly lose N_2O and N_2 to give the $Co(NH_3)_5^{3+}$ intermediate. In the presence of added anions, some $Co(NH_3)_5Y^{2+}$ (where $Y^- = Cl^-$, Br^-, NO_3^-, NCS^-, etc.) was formed. Distinct discrimination in favour of entry of the anion and against that of solvent water was observed. However, the degree of discrimination did not cover a very wide range for different anions, so it was concluded that the postulated intermediate must be very reactive. The results of the study were not very exact, since only a simple spectrophotometric technique was used to determine the relative amounts of $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5Y^{2+}$ formed, the products not actually being separated. Experiments by Pearson and Moore[100] on the spontaneous aquation of the nitratopenta-amminecobalt(III) ion in the presence of thiocyanate ion definitely showed that this reaction did not proceed through a dis-criminating intermediate since $> 98\%$ $Co(NH_3)_5H_2O^{3+}$ was produced followed

by very slow thiocyanate anation.   It seems more likely, therefore,
that the spontaneous aquations of penta-amminecobalt(III) complexes
proceed by an interchange mechanism, as has been proposed for the
reverse anation reaction[50].
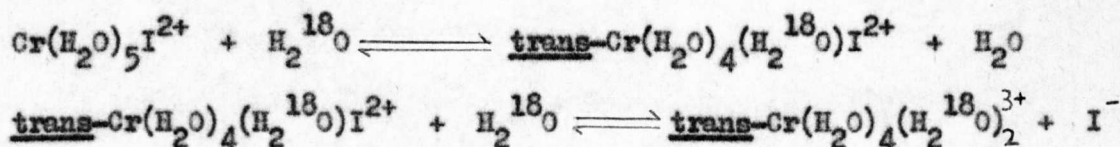
Dolbear and Taube[101] extended the earlier $H_2^{18}O/H_2^{16}O$ fractionation
work of Posey and Taube[98].   Unfortunately, the same fractionation factor
was found in the spontaneous aquation of $Co(NH_3)_5NO_3^{2+}$ as in the induced
aquations $Co(NH_3)_5X^{2+}/Hg^{2+}$ and $Co(NH_3)_5N_3^{2+}/HNO_2$.   Since Pearson and
Moore[100] showed that the mechanism of the spontaneous reaction was
different to that suggested for the induced reactions, it was concluded
that isotope fractionation data are not reliable in determining the
existence of common intermediates.   Other disturbing results presented
in the same paper demonstrated that the extent of incorporation of
nitrate ion into the supposed intermediate was dependent on the method of
generation of the species.   Also, in the presence of either chloride or
bromide ions, the proportions of $Co(NH_3)_5Y^{2+}$ formed during the spontaneous
dissociation of the uncharged trimethylphosphato-ligand (a good leaving
group) from $Co(NH_3)_5OP(OCH_3)_3^{3+}$ were less than those reported earlier[99]
during the reaction of $Co(NH_3)_5N_3^{2+}$ with nitrous acid.   Sargeson
and co-workers[102] repeated some of the earlier work by Haim and Taube[99],
with some additions, using a more sensitive technique for product
evaluation.   The components of product solutions were separated by ion-
exchange, and the concentration of the species present then determined
spectrophotometrically.   Three methods of generating the presumed
intermediate were used, $Co(NH_3)_5N_3^{2+}/HNO_2$, $Co(NH_3)_5OCONH_2^{2+}/HNO_2$, and
$Co(NH_3)_5X^{2+}/Hg^{2+}$ (where $X^- = Cl^-$, Br^-, I^-).   Oxidation of the carbamato-
ligand was rapid and the five co-ordinate intermediate was thought to be
formed by loss of N_2 and CO_2 from a transient species.   The intermediate
was trapped using added anions (e.g. Cl^-, Br^-, NO_3^-, F^-, SO_4^{2-}).   The
same discrimination factor for a particular anion was found for the two
generation methods involving nitrous acid.   The results with Hg^{2+} were,

however, somewhat different and, in the presence of sulphate ion, were found to be complicated by the fact that the rate law of the reaction showed three terms, each with a different order with respect to sulphate ion concentration. It was thought that, using Hg^{2+}, the presence of other anions might also promote a reaction with more than one mechanistic pathway. The results using nitrous acid were, however, tentatively stated to favour the existence of the intermediate $Co(NH_3)_5^{3+}$, though this was considered to be very reactive. Reactions involving penta-amminecobalt(III) complexes with a selectively deuterated ammonia ligand[103] trans to the leaving group showed complete retention of configuration, suggesting that the proposed intermediate would retain a square-pyramidal form, and not rearrange to give a trigonal bipyramid.

By a joint consideration of the various studies described above, it would seem that the existence of the $Co(NH_3)_5^{3+}$ intermediate has not been completely authenticated, and it is certainly very reactive if it does appear. Rapid induced dissociations seem to favour the production of the intermediate, whereas spontaneous aquations would appear to proceed by means of a different mechanism. In contrast to this somewhat confused state of affairs, the evidence for the $Co(CN)_5^{2-}$ intermediate is much more clear-cut. In addition to the excellent kinetic work on the existence of the intermediate, described in Chapter 1, Haim and co-workers have undertaken some competition experiments[45]. The acid-catalysed aquation of $Co(CN)_5N_3^{3-}$ in the presence of thiocyanate produces some $Co(CN)_5SCN^{3-}$ in addition to $Co(CN)_5OH_2^{2-}$. The discrimination factor in favour of the entry of thiocyanate ion is the same as that obtainable from kinetic studies of the anation reaction of $Co(CN)_5OH_2^{2-}$.

The first direct evidence for the involvement of a five co-ordinate intermediate in the reaction of a chromium(III) complex was provided by Ardon[104]. In the spontaneous aquation of $Cr(H_2O)_5I^{2+}$ considerable amounts of $Cr(H_2O)_5Y^{2+}$ were formed in the presence of either Cl^- or Br^-,

but very little acceleration of the rate of disappearance of the reactant complex was observed.   Retardation of the reaction rate by added iodide ion was, however, found.   Ardon interpreted his results as confirming the existence of the intermediate $Cr(H_2O)_5^{3+}$ with added anions and solvent water competing in the formation of products.   An alternative explanation for Ardon's results was presented by Moore et al[61].   The aquation of $Cr(H_2O)_5I^{2+}$ in $H_2^{18}O$ produced a hexa-aquo product containing two labelled water molecules, instead of one as expected by Ardon's mechanism.   The _trans_ activating ability of the iodo-ligand was invoked and thought to promote exchange of the _trans_ water molecule in the complex prior to hydrolysis:

$$Cr(H_2O)_5I^{2+} + H_2^{18}O \rightleftharpoons \underline{trans}\text{-}Cr(H_2O)_4(H_2^{18}O)I^{2+} + H_2O$$

$$\underline{trans}\text{-}Cr(H_2O)_4(H_2^{18}O)I^{2+} + H_2^{18}O \rightleftharpoons \underline{trans}\text{-}Cr(H_2O)_4(H_2^{18}O)_2^{3+} + I^-$$

Ardon's results can then be explained by the mechanism:

$$Cr(H_2O)_5I^{2+} + Y^- \rightleftharpoons \underline{trans}\text{-}Cr(H_2O)_4YI^+ + H_2O$$

$$\underline{trans}\text{-}Cr(H_2O)_4YI^+ + H_2O \rightleftharpoons Cr(H_2O)_5Y^{2+} + I^-$$
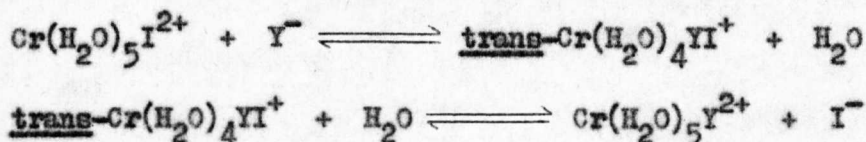
However, since no direct evidence for the di-halo-intermediate was found, Ardon's postulate is not completely discredited.   Also, the intermediate $Cr(H_2O)_5^{3+}$ might possibly occur in reactions other than spontaneous aquation.

In a recent paper[105], published after the present study was completed, Ferraris and King have presented evidence for the formation of a common intermediate, believed to be $Cr(H_2O)_5^{3+}$, in water-methanol solvent by means of the following reactions:

$$Cr(H_2O)_5X^{2+} + M^{n+} + Z \longrightarrow Cr(H_2O)_5Z^{3+} + MX^{(n-1)+}$$

$$Cr(H_2O)_5N_3^{2+} + HONO + H^+ + Z \longrightarrow Cr(H_2O)_5Z^{3+} + N_2 + N_2O + H_2O$$

$$Cr(H_2O)_5I^{2+} + Z \longrightarrow Cr(H_2O)_5Z^{3+} + I^- \underline{\qquad}3(i)$$
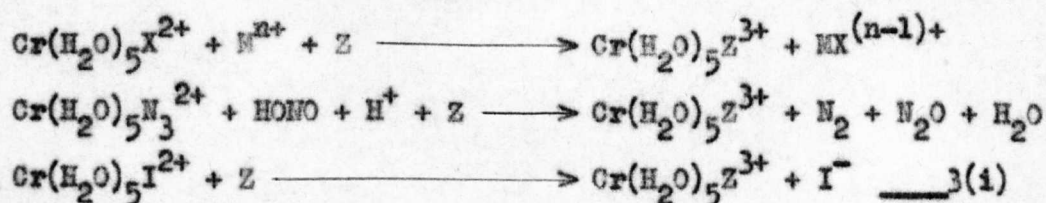
where $X^- = Cl^-$, Br^-, I^-; $M^{n+} = Ag^+$, Hg^{2+}, Tl^{3+}; $Z = H_2O$ or CH_3OH.

The same solvent fractionation factor, for a particular methanol-water composition, was found for all three methods of generating the supposed intermediate. In reaction 3(i), the methanol content of the product increased with time, because of the labilising ability of the iodo-ligand mentioned previously, but this difficulty was resolved by taking a solvent fractionation factor extrapolated back to zero reaction time.

In this work the possible involvement of a D process in the induced dissociation of a penta-aquochromium(III) complex was investigated, using added anions in an attempt to trap the intermediate. Since various complications can accompany metal-ion catalysed dissociations, as mentioned previously, it seemed wise to avoid this method. A consideration of the relative merits of the acid catalysed dissociation of a basic ligand and the in situ oxidation of a co-ordinated group favoured the latter. The nitrous acid oxidation of a co-ordinated azido-group was known to be rapid[99] which would help to overcome problems due to partial aquation of the expected products, $Cr(H_2O)_5Y^{2+}$, before separation and analysis.

As an adjunct to the competition experiments, the kinetics of the reaction :

$$Cr(H_2O)_5N_3^{2+} + HONO + H^+ \longrightarrow Cr(H_2O)_6^{3+} + N_2O + N_2 \qquad 3(ii)$$
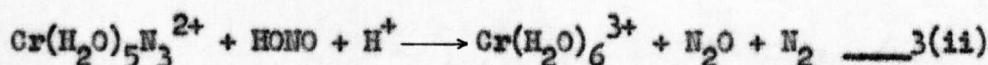
were studied in perchlorate and mixed perchlorate-chloride media, to compare the mechanism with those reported for the azidopenta-amminecobalt(III)[99] and rhodium(III)[106] systems. Since this work was carried out, a further kinetic study of reaction 3(ii) has been reported[107], the results of which will be discussed later.

3.2. Experimental

(a) Preparation of the Azidopenta-aquochromium(III) Ion

Solutions of $Cr(H_2O)_5N_3^{2+}$ in ca. 1N perchloric acid were prepared and analysed by a published method[37]. The visible and U.V. spectra of the samples agreed excellently with that reported[37]. Some samples were

stored by freezing in dry ice, but later it was discovered that solutions could be preserved at 273 K for several days before detectable aquation became apparent.

(b) Kinetics

For the kinetic study of reaction 3(ii) the stopped-flow technique was employed with a monitoring wavelength of 272 nm, a peak maximum in the spectrum of $Cr(H_2O)_5N_3^{2+}$ ($E_M = 3740$). The other absorbing species present were HNO_2 (E_M ca. 4) and the product $Cr(H_2O)_6^{3+}$ (E_M ca. 5). A complex concentration of approximately 5×10^{-5}M was found to be suitable. Other reagent concentrations were in the ranges, $[H^+]$ @ 0.01 to 0.5M, $[HNO_2]$ @ 0.001 to 0.04M, and $[Cl^-]$ @ zero, or 0.01 to 0.49M. Acidic complex solutions were mixed with neutral nitrite solutions, so that decomposition of HNO_2 was not a problem.

(c) Competition Experiments

Preliminary experiments were carried out using added chloride or bromide ions as scavengers under similar conditions of temperature, acidity, and added anion concentration as those used by Ardon[104]. No direct spectrophotometric evidence for the production of $Cr(H_2O)_5Y^{2+}$ was found, spectra of product solutions agreeing with that of $Cr(H_2O)_6^{3+}$, within experimental error. Since quite large concentrations of excess HNO_2 (up to 0.05M) were present in the product solutions of preliminary experiments, the possible effect on the subsequent aquation of $Cr(H_2O)_5Y^{2+}$ was investigated. Catalysis of the aquation reaction was, indeed, observed and later experiments were carried out at low temperatures, with little excess HNO_2, to minimise this effect. The experimental conditions used subsequently were such that, during the time between formation and separation, the aquation of the $Cr(H_2O)_5Y^{2+}$ product was negligible. The unexpected effect of nitrous acid in accelerating the rates of aquation of chromium(III) complexes will be examined further in Chapter 4.

It was necessary to employ high scavenger concentrations to produce sufficiently large amounts of $Cr(H_2O)_5Y^{2+}$ (where $Y^- = Cl^-$, Br^-, SCN^-, HSO_4^-) for accurate analysis. Anions were added as their sodium salts, except for HSO_4^-, for which sulphuric acid was employed. The acidity in the bisulphate experiment was made deliberately high so that $<4\%$ was in the form of SO_4^{2-} (calculated using known equilibrium constants[16]). All experiments were carried out at ca. 273 K, and added anion concentration kept in excess by the addition of sodium nitrite solution dropwise to a stirred acidic mixture of azido-complex and scavenger. In every case but one the reacted solution was pale blue; however, in the thiocyanate ion experiment a reddish-brown colouration slowly developed, apparently due to the oxidation of SCN^- to $(SCN)_2$[101]. Since ca. 50% excess HNO_2 was employed, this side reaction should not have interfered with the competition experiment because, under the conditions used, reaction 3(ii) was complete in the time taken for the addition of the reagent. Approximately one minute after nitrite addition the solution was diluted with sufficient ice-cold water to render the ionic strength less than 0.1, and the products immediately separated using cation-exchange.

A pre-washed (0.02M $HClO_4$) column (20 X 1cm) of Dowex 50WX8 (50-100 mesh, H^+ form) resin was employed, maintained at ca. 273 K by ice-water circulating through a surrounding jacket. Solutions were loaded at a slow drop rate (ca. 1 per second), then excess nitrous acid and scavenger ion were washed off using 0.05M $HClO_4$ (ca. five bed volumes). Chromium species of charge less than +3 were eluted with 1M $HClO_4$ (ca. 300 ml). Dilute solutions of the chloro- and bromopenta-aquochromium(III) complexes were identified by their visible spectra, using 10 cm pathlength cells in the Cary 14 spectrophotometer, which was fitted with a 0 - 0.2 absorbance slidewire. The eluted solutions were too dilute to be directly assayed spectrophotometrically with sufficient accuracy, so they were oxidised to chromate ion and analysed

as described in Chapter 2.   A further check on the chloro-complex was possible by estimating the oxidised solution for chloride ion content, using the chloride ion selective electrode.   Chloride : chromium ratios of (1.00 ± 0.05) : 1 were observed.   The $Cr(H_2O)_6^{3+}$ formed was analysed by removing the resin from the column, extracting several times with warm alkaline H_2O_2, and determining the resulting CrO_4^{2-} as described in Chapter 2.   The total recovery of all chromium species was close to 100% in every experiment.

3.3.   Kinetic Results and Discussion

The stoicheiometry of the reaction was assumed to be the same as that found for the azidopenta-amminecobalt(III) ion[99], and is represented by equation 3(ii).   The only Cr(III) products were confirmed by cation exchange experiments to be $Cr(H_2O)_6^{3+}$ and (in the presence of added Cl^-) a little $Cr(H_2O)_5Cl^{2+}$.   Average values (from 2 – 4 experiments) of the pseudo first-order rate constants, k_{obs}, are collected in Table 1. In the absence of chloride ion, values of $k_{obs}/[HNO_2]/[H^+]$ are constant and the rate law is :

$$-d[Cr(H_2O)_5N_3^{2+}]/dt = k_1[H^+][HNO_2][Cr(H_2O)_5N_3^{2+}] \underline{\quad\quad} 3(iii)$$

The excellent first order behaviour with respect to $[H^+]$ and $[HNO_2]$ can be seen in Figures 13 and 14.   At 298.1 K, $k_1 = (2.49 \pm 0.11)$ $\times 10^3 M^{-2} s^{-1}$.   This rate law is confirmed by the work of Thompson and Kaufmann[107], whose k_1 value of $2.40 \times 10^3 M^{-2} s^{-1}$ is in excellent agreement with that reported here.   Their study was carried out at much lower nitrous acid concentrations using a conventional technique, and the ranges of $[H^+]$ and $[HNO_2]$ covered were somewhat less than in the present work.   The rate law is the same as has been found for the reaction of $Co(NH_3)_5N_3^{2+}$ [99] and is similar to that reported for $Rh(NH_3)_5N_3^{2+}$ [106].   The values of k_1 are very similar in all three cases, which is to be expected since the reactions involve attack on a co-ordinated ligand which is bound to metal ions of the same oxidation state

TABLE 1

Kinetic data for reaction 3(ii) at 298.1 K in
perchlorate and mixed perchlorate-chloride media

$I = 1.0$ (NaClO$_4$); $[Cr(H_2O)_5N_3^{2+}]$ ca. 5×10^{-5}M.

$[H^+]/M$ [a]	$10^2[HNO_2]/M$ [b]	$[Cl^-]/M$	k_{obs} s^{-1}	$10^{-3}k_{obs}/[H^+][HNO_2]$ M^{-2}s^{-1}
0.50	0.10	-	1.20	2.40
0.50	0.20	-	2.39	2.39
0.50	0.40	-	4.85	2.43
0.50	1.00	-	12.0	2.40
0.50	2.00	-	23.9	2.39
0.50	4.00	-	50.3	2.51
0.20	1.00	-	4.85	2.43
0.10	1.00	-	2.62	2.62
0.05	1.00	-	1.33	2.66
0.02	1.00	-	0.511	2.55
0.01	1.00	-	0.262	2.62
0.50	1.00	0.49	132	26.4
0.50	1.00	0.20	80.8	16.2
0.50	1.00	0.10	50.3	10.1
0.50	1.00	0.05	32.6	6.52
0.50	1.00	0.02	20.5	4.10
0.50	1.00	0.01	16.4	3.28
0.01	1.00	0.10	1.02	10.2
0.50	0.10	0.10	4.54	9.08

(a) Free acid concentration allowing for the amount consumed in forming HNO$_2$.

(b) The known[114] pK$_a$ of HNO$_2$ was used to estimate $[HNO_2]$.

FIGURE 13

Kinetics of reaction 3(ii)

at 298.1 K and I = 1.0 ($NaClO_4$).

$[HNO_2] = 0.01M$

$k_{obs}/[HNO_2] \, (M^{-1} s^{-1})$

$[H^+] M$
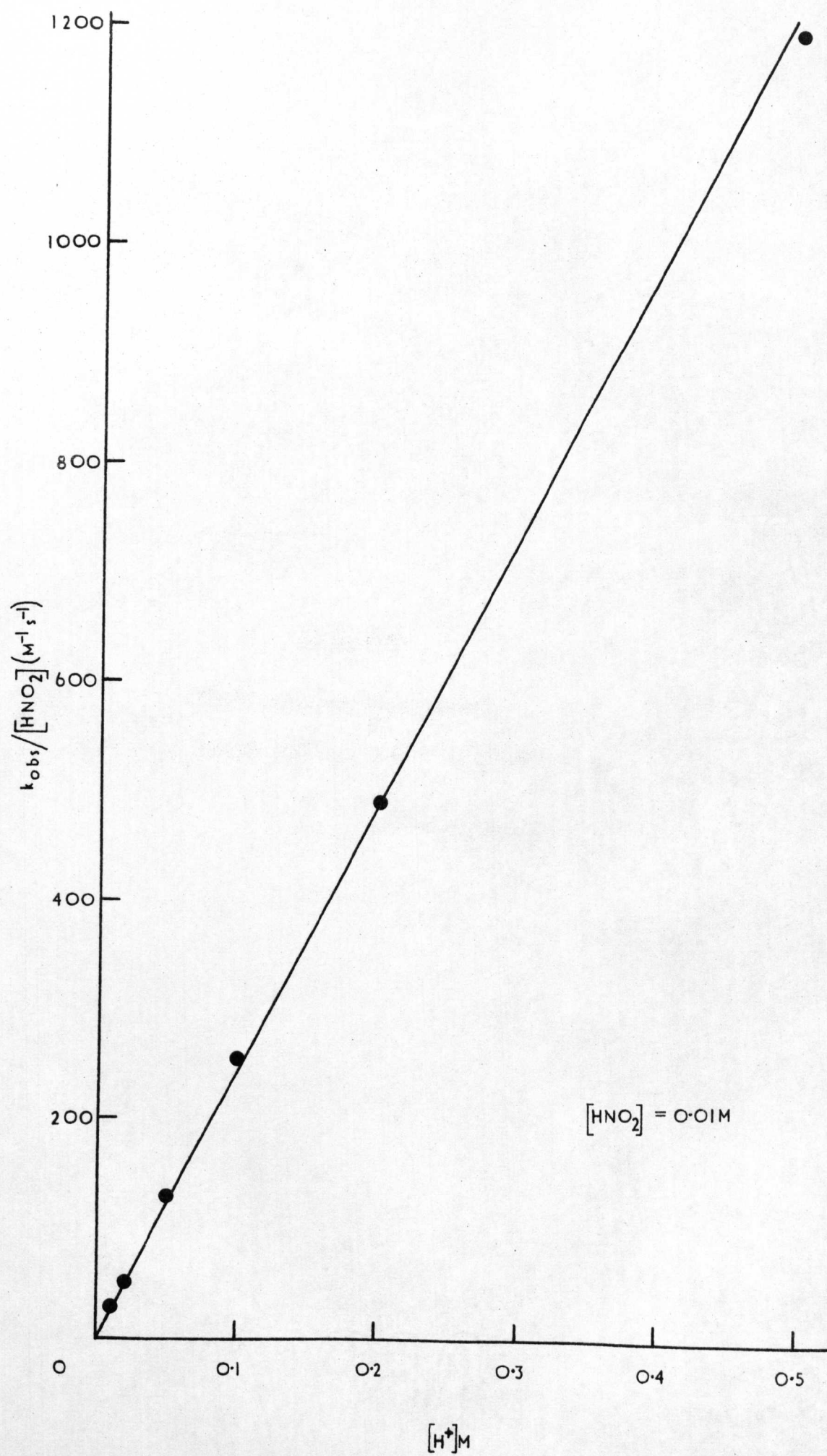
FIGURE 14

Kinetics of reaction 3(ii)
at 298.1 K and I = 1.0 ($NaClO_4$).
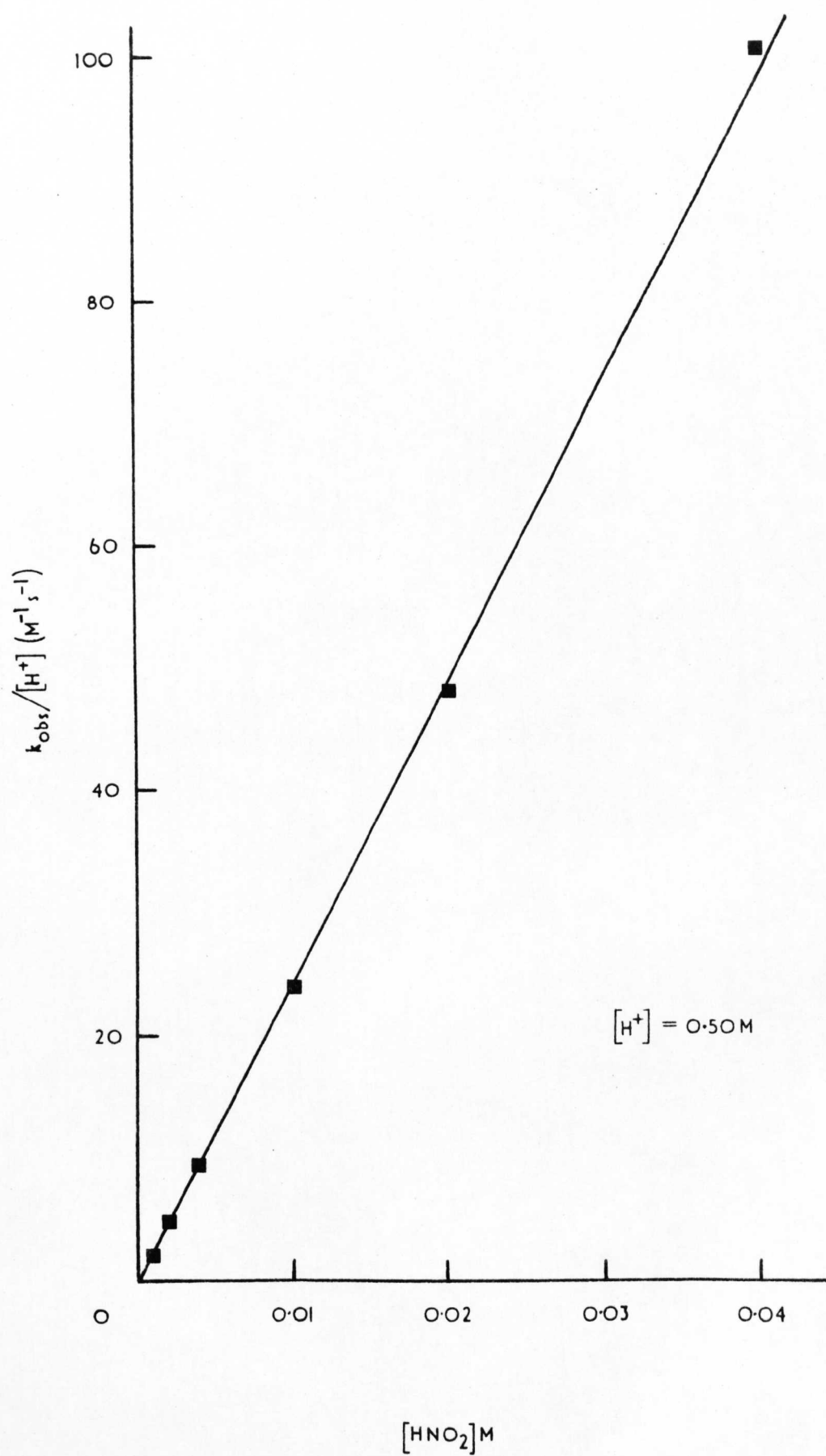
The y-axis is labeled $10^6 \left(k_{obs}/\left[H^+\right]\left[HNO_2\right] - k_1 \right)^{-1}$ $(M^2 s)$ with gridline values 2, 4, 6, 8, 10, 12.

The x-axis is labeled $\left[Cl^-\right]^{-1}$ (M^{-1}) with gridline values 0, 20, 40, 60, 80, 100.
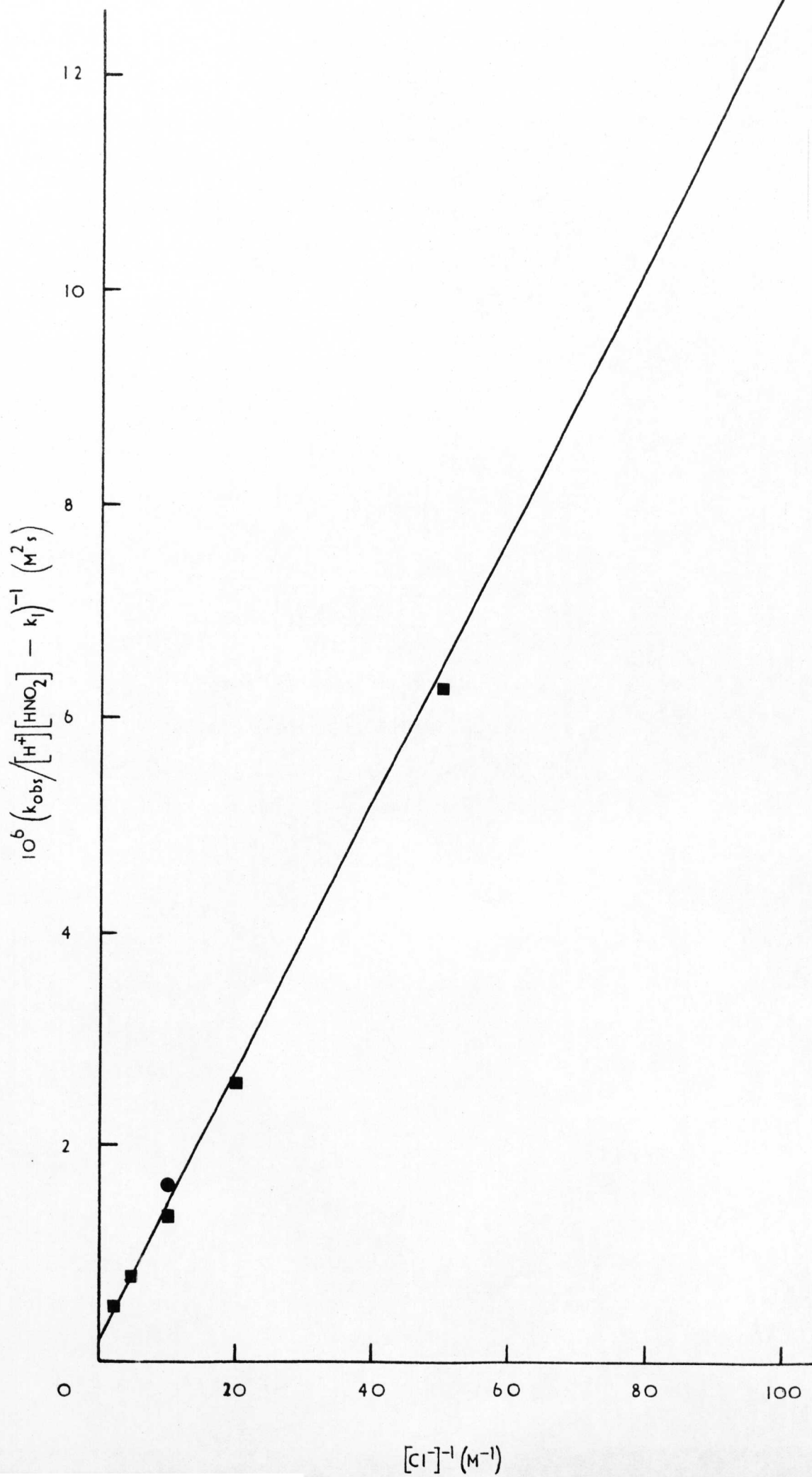
in complexes of the same overall charge. No evidence was found for a reaction pathway involving N_2O_3, as with $Rh(NH_3)_5N_3^{2+}$ [106]. However, much higher acid concentrations were used in the present study, so that there is no reason why such a pathway should not appear at lower acidities.

Reaction 3(ii) is considerably faster in the presence of chloride ion, but seems to approach a limiting rate as $[Cl^-]$ increases, as has been observed for this reaction by Thompson and Kaufmann[107], and also for the corresponding reaction of $Co(NH_3)_5N_3^{2+}$ [99]. The same type of rate law was deduced as that reported[99] for $Co(NH_3)_5N_3^{2+}$:

$$-d[Cr(H_2O)_5N_3^{2+}]/dt = k_{obs}[Cr(H_2O)_5N_3^{2+}]$$

where $k_{obs} = ((k_1 + k_2[Cl^-])/(1 + k_3[Cl^-]))[H^+][HNO_2]$ _____3(iv)

Rearrangement of 3(iv) gives:

$$((k_{obs}/[H^+][HNO_2]) - k_1)^{-1} = k_3/(k_2-k_1k_3) + ((k_2-k_1k_3)/[Cl^-])^{-1}$$

A plot of the left side of this equation against $[Cl^-]^{-1}$ is linear, as shown in Figure 15, and weighted linear least-squares analysis of the results using computer program R002/01 (Appendix 2) gives $k_2 = (8.3 \pm 0.5) \times 10^4$ $M^{-3}s^{-1}$ and $k_3 = 1.3 \pm 0.3$ M^{-1}. Analysis of the results of the reaction of $Co(NH_3)_5N_3^{2+}$ with HNO_2 and Cl^- (Table II of ref. 99) gives very similar values for k_2 (1.5×10^5 $M^{-3}s^{-1}$) and k_3 (0.49 M^{-1}).

The following mechanism is consistent with equations 3(iii) and (iv), and with previous work[99]:

$$H^+ + HNO_2 \xrightleftharpoons{K'} H_2NO_2^+, \text{ rapid}$$

$$H_2NO_2^+ + Cl^- \xrightleftharpoons{K''} NOCl + H_2O, \text{ rapid}$$

$$Cr(H_2O)_5N_3^{2+} + H_2NO_2^+ \xrightleftharpoons[k_{-4}]{k_4} Cr(H_2O)_5N_4O^{3+} + H_2O$$

$$Cr(H_2O)_5N_3^{2+} + NOCl \xrightleftharpoons[k_{-5}]{k_5} Cr(H_2O)_5N_4O^{3+} + Cl^-$$

$$Cr(H_2O)_5N_4O^{3+} \xrightarrow{\quad k_6 \quad} products$$
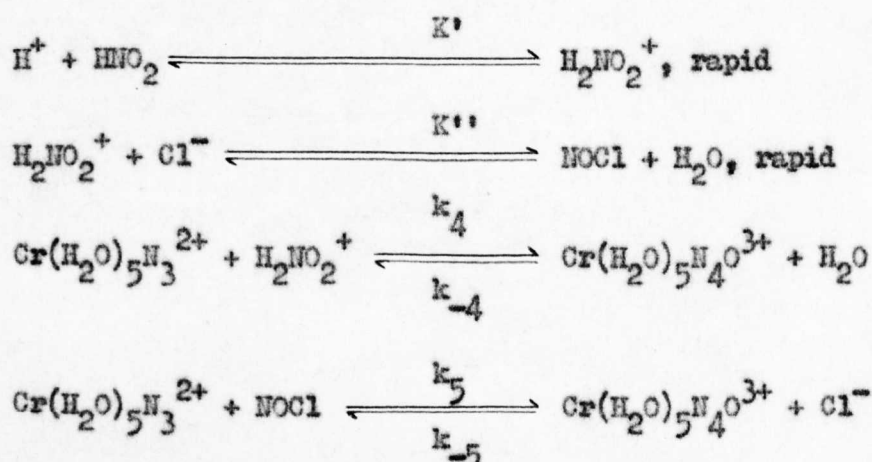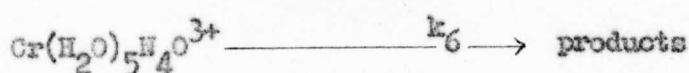
A mechanism involving NO^+ rather than $H_2NO_2^+$ would be kinetically indistinguishable. H_2NO_2 is, however, preferred since Stedman[108] has shown that, in the oxidation of HN_3 by nitrous acid, a mechanism involving $H_2NO_2^+$ is predominant in excess perchloric acid. Stedman also demonstrated that the species N_4O is an intermediate in the oxidation of hydrazoic acid by nitrous acid. Application of the steady-state approximation to $Cr(H_2O)_5N_4O^{3+}$ gives :

$$-d[Cr(H_2O)_5N_3^{2+}]/dt = \frac{k_6(k_4K' + k_5K'K''[Cl^-]/[H_2O])[H^+][HNO_2][Cr(H_2O)_5N_3^{2+}]}{k_6 + k_{-4}[H_2O] + k_{-5}[Cl^-]}$$

In the absence of chloride ion, the equation reduces to 3(iii) with $k_1 = k_6k_4K'/(k_{-4}[H_2O] + k_6)$. Comparison with 3(iv) shows that $k_2 = k_5K'K''/((k_{-4}[H_2O] + k_6)/[H_2O])$ and $k_3 = k_{-5}/(k_{-4}[H_2O] + k_6)$.

3.4. Competition Experiments - Results and Discussion

As outlined in the introduction to this chapter, if it is assumed that the formation of $Cr(H_2O)_5Y^{2+}$ is via a five co-ordinate intermediate, a discrimination factor in favour of the entry of the added anion and against that of solvent water can be defined thus :

$$F = [Cr(H_2O)_5Y^{2+}][H_2O]/[Cr(H_2O)_6^{3+}][Y^-]$$

In this study, for $[H_2O]$ the formal concentration of water, 55.5M, will be used. This definition for F assumes that the ratio $[H_2O]/[Y^-]$ in the vicinity of the intermediate is the same as in the bulk solution, an assumption which is not necessarily correct[43]. On this scale, a value of $F = 1$ indicates no discrimination by the intermediate. The conditions of the competition experiments and the values of F obtained are listed in Table 2. A comparison with the results of Ardon[104] ($F = 13.4$ for Cl^-, and 12.6 for Br^-) shows that either the alternative explanation[61] of Ardon's results is correct or the same intermediate is

TABLE 2

Estimates of the Cr(III) product distributions
For reaction 3(ii) in the presence of scavenger
anions, Y⁻, at ca. 273 K

Conditions

Expt. No.	Y⁻	$[Y^-]/M$	$10^3[Cr(H_2O)_5N_3^{2+}]/M$	$[H^+]/M$	$10^2[HNO_2]/M$	I
1	ClO_4^-	2.78	11.2	0.95	1.82	2.8
2	Cl^-	2.00	10.9	0.95	1.82	3.0
3	Cl^-	5.00	11.6	0.95	1.82	6.0
4	Br^-	2.00	10.7	0.95	1.82	3.0
5	NCS^-	1.59	4.35	0.38	0.72	3.0
6	HSO_4^-	2.00	9.70	2.9	1.62	3.0

Results

Expt. No.	Y⁻	10^4 No. mols. reactants and products			% Cr recovered	F
		$Cr(H_2O)_5N_3^{2+}$	$Cr(H_2O)_6^{3+}$	$Cr(H_2O)_5Y^{2+}$		
1.	ClO_4^-	6.15	6.17	none	100.4	0
2	Cl^-	6.02	5.54	0.46	99.7	2.3
3	Cl^-	6.40	5.31	1.10	100.2	2.3
4	Br^-	5.90	5.43	0.44	99.6	2.2
5	NCS^-	3.70	3.18	0.46	98.5	5.0
6	HSO_4^-	4.80	4.10	0.70*	100.0	4.7

* $[Cr(H_2O)_5SO_4^+]$

not involved in reaction 3(ii) and the spontaneous aquation of the iodopenta-aquochromium(III) ion. Thompson and Kaufmann[107] attempted competition experiments of a similar nature to those reported here, but using much lower added anion concentrations. They were unable to accurately determine the amounts of $Cr(H_2O)_5Y^{2+}$ formed, but their estimated results are much more in line with those of this study than with Ardon's[104]. It seems likely that, if $Cr(H_2O)_5^{3+}$ is an intermediate in the aquation of penta-aquochromium(III) complexes, it does not have the ability to discriminate between nucleophiles which Ardon's results first seemed to suggest. Additional evidence for this has resulted from studies of the aquation of $Cr(H_2O)_5SCN^{2+}$ (the S-bonded complex ion) in 0.8M Cl^-, very little $Cr(H_2O)_5Cl^{2+}$ being found in the products[109]. The low values for F found in the present study for the thiocyanate and bisulphate ions, as well as the value of F = 0.55 reported for methanol[105], are also in line with this view. The F values of NCS^- and HSO_4^- are approximately twice as large as those of Cl^- and Br^-, but the variation, and discrimination against solvent water, are much smaller than normally experienced in cases where five co-ordinate intermediates are well established[44,46,48].

It is possible that an I_d mechanism could equally well explain the results of this study, with the added anion Y^- entering the inner-sphere as N_2 and N_2O dissociate from $Cr(H_2O)_5N_4O^{3+}$, after the prior formation of an ion-pair. Values of ion-pair formation constants are obviously unobtainable for the transient species $Cr(H_2O)_5N_4O^{3+}$ but should be similar to those of $Cr(H_2O)_6^{3+}$. However, ion-pair constants are not even available for $Cr(H_2O)_6^{3+}$ under the conditions used in this study and it would be somewhat naive to try to estimate values theoretically[11], because of the high ionic strengths obtaining in the experiments. Because of the high added anion concentrations employed, it would seem possible that a small proportion of $Cr(H_2O)_5N_4O^{3+}$ could be in the form

of an ion-pair, and, for example, outer-sphere association of less than 13% in 1.59M thiocyanate ion could explain the results obtained in terms of an interchange mechanism. Postmus and King[110] report an ion-pair formation constant for $Cr(H_2O)_6^{3+} \cdot NCS^-$ of ca. 1 at I = 1.2, which could represent an ion-pair population as high as 60% under the conditions used in this study. The discrimination factors observed for the various anions could thus be dependent on their outer-sphere association constants, which for singly charged anions with complex ions such as $Co(NH_3)_5OH_2^{3+}$ [29] are thought to be very similar. This would explain the narrow range of discrimination factors observed. Another possibility for an interchange mechanism is a concerted process with the electrophile NOY placing Y^- on the central metal ion as it attacks the co-ordinated azido group and displaces N_2O and N_2. A difficulty with this interpretation is the fact that, at the high added anion concentrations employed in these experiments, almost 100% of the reaction goes via the pathway involving NOY rather than $H_2NO_2^+$. On this basis, much higher discrimination factors should be expected for added anions than those which are actually observed.

Perhaps the best evidence for the involvement of an intermediate is the fact that the same discrimination factor was found for two quite different added chloride ion concentrations (see Table 2). Significant ion-pair formation should result in a decrease in F with increased anion concentration, an effect which has been described previously[99], while a value of F insensitive to added anion concentration is more in line with the existence of an intermediate. However, if a genuine five co-ordinate species is involved in the reaction studied here, since it has been shown to possess little facility to discriminate between anions in solution, it would seem to be a little surprising that no evidence for the incorporation of perchlorate ion to form the known complex[111], $Cr(H_2O)_5ClO_4^{2+}$, was observed. Even though the aquation of this complex

would be more rapid than the acidopenta-aquochromium(III) complexes formed with the other anions studied, no sign of its production was detected in the experiment in which it was sought, even though a high perchlorate ion concentration (2.8M), was employed.

If it is assumed that the aquation of penta-aquochromium(III) complexes proceed by means of a D mechanism, a value of F can be estimated by the method of Haim and Taube[99]. In the absence of ion-pairing, the overall equilibrium constant, K_f, for the formation of the complex is given by $K_f = k_e k_x / k_w k_a$, where rate constants are defined in 3(v) and 3(vi) :

$$Cr(H_2O)_6^{3+} \underset{k_w}{\overset{k_e}{\rightleftharpoons}} Cr(H_2O)_5^{3+} + H_2O \underline{\quad\quad} 3(v)$$

$$Cr(H_2O)_5^{3+} + X^- \underset{k_a}{\overset{k_x}{\rightleftharpoons}} Cr(H_2O)_5 X^{2+} \underline{\quad\quad} 3(vi)$$
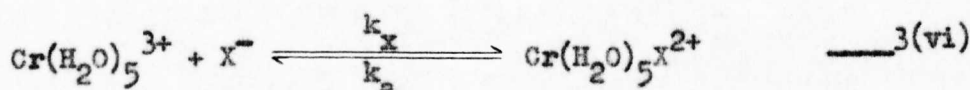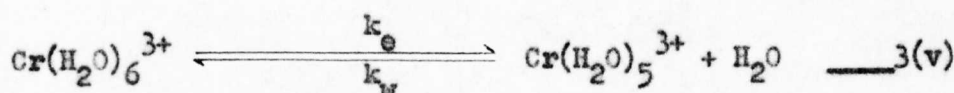
The quotient k_x/k_w gives a measure of the discrimination of the intermediate for the anion and against solvent water. Thus $F = k_x/k_w = K_f k_a [H_2O]/k_e$. The formal concentration of water (55.5M) is included in the quotient since published values of K_f do not involve this quantity. Using a value[112] of $k_e = 3 \times 10^{-6} s^{-1}$, which is the total exchange rate of all six water molecules in $Cr(H_2O)_6^{3+}$, and values of K_f and k_a [30] listed in Table 3, the approximate values of F derived at 298.1 K and I = 1.0 are 0.56 for Cl⁻, 0.16 for Br⁻, and 31 for NCS⁻.

TABLE 3

Anion	K_f (M⁻¹)	k_a (s⁻¹)
Cl⁻	0.110	2.76×10^{-7}
Br⁻	2.24×10^{-3} *	3.89×10^{-6}
SCN⁻	182	9.12×10^{-9}

* Value at I = 2.0

The calculated F factors indicate the wider range of discrimination that might be expected for the five co-ordinate intermediate, compared to the results obtained in this study. It is apparent that either the mechanisms of the spontaneous and induced aquations of acidopenta-aquochromium(III) complexes are different or that a different intermediate to $Cr(H_2O)_5^{3+}$ is involved in this work.

3.5. Conclusions

It has been shown that the discrimination factors obtained for the ions Cl^- and Br^- in the induced aquation of $Cr(H_2O)_5^{2+}$ are different to those reported during the spontaneous aquation of $Cr(H_2O)_5 I^{2+}$ [104]. Since the spontaneous aquation has been shown by both Moore[61] and King[105] to be complicated by the labilising ability of the iodo ligand, it might be instructive to repeat Ardon's work using the method of King[105], by determining discrimination factors at different extents of reaction, and extrapolating back to zero time. If the extrapolated values of F were the same as found in this work, it would be good evidence for a common intermediate, but, as Taube has pointed out[101], not conclusive evidence. Configuration changes during the induced aquations of complexes of the type cis and trans- $Cr(H_2O)_4 XL^{n+}$ are another possibility for study, but the danger here is that the intermediate will not now be the same, and it could be invalid to take the possible existence of $Cr(H_2O)_4 L^{n+}$ as confirming that of $Cr(H_2O)_5^{3+}$.

The comparative lack of discrimination between anions and water that is exhibited by the postulated intermediate $Cr(H_2O)_5^{3+}$ may indicate that it can seek no further than its own solvation sheath for a reaction partner. Thus a half-way case could be described between interchange and a (comparatively) stable five co-ordinate intermediate such as $Co(CN)_5^{2-}$, that of an intermediate possessing a finite lifetime but only being able to survive some outer-sphere rearrangement. King's results[105] might be explained by this model if the outer-sphere

population of, say, $Cr(H_2O)_6^{3+}$ were known in mixed methanol-water solvents. Langford[43] has determined the relative population of the outer-sphere of $Cr(NCS)_6^{3-}$ in acetonitrile-water mixtures by an NMR technique. The outer-sphere was found to be saturated with CH_3CN in a bulk solvent having as low as 20% acetonitrile content. Similar behaviour of $Cr(H_2O)_6^{3+}$ in H_2O/CH_3OH mixtures would obviously disprove the above suggestion, and indicate that $Cr(H_2O)_5^{3+}$ seeks beyond its outer-sphere for a reaction partner.

In view of the apparent high reactivity and poor discrimination exhibited, further investigation of the possible existence of the intermediate $Cr(H_2O)_5^{3+}$ was curtailed since it is doubtful if definitive evidence could be obtained. Should a different method of attempted generation of the intermediate give the same discrimination factors as the method used in this study, it would still not be conclusive evidence. The existence of the somewhat analogous species $Co(NH_3)_5^{3+}$ is still debatable, even though larger discrimination factors for added anions have been deduced[102] than those reported in this study. Also, Spees et al[113] have recently reported some theoretical calculations which show that a transition state of octahedral wedge structure has the lowest energy for reactions of chromium(III) complexes. This structure probably best matches an I process.

CHAPTER 4

The Nitrous Acid Catalysis of Aquations
of Halo-aquochromium(III) complexes

4.1. Introduction

The unusual effect of nitrous acid in catalysing the aquations of halopenta-aquochromium(III) complexes, as mentioned in Chapter 3, merited further investigation in an attempt to deduce the mechanism of the inter- action. Excluding heterogeneous catalysis and redox processes, there appear to be four ways of catalysing the rate of substitution of a metal complex:

1. Outer-sphere association by the catalyst

2. Direct attack by the catalyst on the leaving group

3. Co-ordination of the catalyst

4. Reaction of the catalyst with a co-ordinated, non-leaving ligand.

Considering category 1, the effect of ion-pairing on the substitution rates of complexes is a very general one[1c]. For example, the acceleration by anions of the rates of aquation of halopenta-amminechromium (III) complexes has been well studied[115-6]. The effect of nitrous acid on the aquation rates of halo-aquochromium(III) ions does not, however, appear to be of this type, since, under the acidic conditions employed, very little NO_2^- would be present, the predominant species being HNO_2. Also, the magnitude of the catalysis is much greater than would be expected for an outer-sphere association effect, since the aquation rate of $Cr(H_2O)_5Br^{2+}$ (@ ca.10^{-3}M) is increased by a factor of ten in the presence of only 0.01M $[HNO_2]$, at pH 1 and 318 K. Furthermore, catalysis by HNO_2 of the rate of aquation of $Cr(NH_3)_5Br^{2+}$ is not evident, as will be shown later.

Some reactions of category 2, have been mentioned in Chapters 1 and 3. Examples include the labilisation of highly-basic ligands by protonation[35-41], the induced dissociation of halo-ligands using metal

ions such as Ag^+, Hg^{2+}, and Tl^{3+} [98,101-2,105] and the oxidation of a co-ordinated azido-group by means of nitrous acid [99,101-2,105-7].

The efficacy of I_2 in catalysing the aquation of $Cr(H_2O)_5I^{2+}$ by a process of this type has also been demonstrated [117]. However, direct attack of an electrophile such as NO^+ or $H_2NO_2^+$ on the halo-ligand would not appear to be responsible for the observed catalysis, since the aquation rate of $Cr(NH_3)_5Br^{2+}$ is not affected.

Catalysis by a category 3 process is unlikely for octahedral complexes where dissociative activation is predominant, but might be expected for species with a lower co-ordination number where associative substitution mechanisms occur. Catalysis by nitrous, boric, acetic and trifluoracetic acids has been reported [118-9] for the substitutions of some square-planar platinum(II) complexes. The mechanism is thought to involve the replacement by an undissociated acid molecule, HA, of a solvent molecule on the elongated z-axis perpendicular to the plane of the complex. It is postulated that HA removes electronic charge from the central metal-ion, by means of a π-orbital interaction, thus encouraging attack by a nucleophile. That acetic and boric acids have but little effect on the aquation rates of halo-aquochromium(III) complexes will be demonstrated later.

It would appear that a category 4 catalytic process can only be efficient if the catalyst-ligand reaction is more rapid than the substitution process which is catalysed [120]. Such a situation is more likely for inert complexes, for example those of chromium(III). Possibly the most widespread example of a type 4 mechanism is base catalysis. The rapid loss of a proton from a non-leaving ligand of a complex to form the more labile conjugate base is thought to be the explanation for the catalysis, as has been mentioned in Chapter 1. Basolo and Hammaker [121] have shown that the formations of nitrito-complexes are rapid since they

involve O-nitrosation of a co-ordinated aquo-ligand, and hence no
fission of the metal-oxygen bond. It was demonstrated in the same work
that the O-bonded nitrito-ligand is the stable form in chromium(III)
complexes, no evidence being found for rearrangement to form the N-
bonded nitro-isomer as occurs in the analogous complexes of cobalt(III),
rhodium(III), iridium(III) and platinum(IV). Evidence for the belief
that nitrito-intermediates are involved in the catalysis by HNO_2 of
the aquations of halo-aquochromium(III) complexes will be presented in
due course.

Beck[120] has ascribed the catalysis by CO_2 of the anation of $Cr(H_2O)_6^{3+}$
by SCN^- at pH 4.2 to the formation of carbonato-intermediates. Earley
and Alexander[122] have also reported catalysis by CO_2, of the oxygen
exchange rate of $Cr(NH_3)_5OH^{2+}$. These workers also attribute the effect
to the formation of a carbonato-intermediate, by a rapid process avoiding
Cr-O bond fission. In the same paper, the authors state that the
catalytic activity of CO_2 is a general one for the substitution processes
of chromium(III) complexes, but the further studies promised have not
yet appeared in the literature. Since CO_2 was not rigorously excluded
from the solutions used in the present work, it might be that dissolved
carbon dioxide could have had some small effect on the observed reaction
rates. However, perusal of the data of Early and Alexander[122] shows
that the catalytic effect of CO_2 lessens with decreasing pH. At pH 1.49,
which corresponds approximately with the lowest acidity used in the
current study, the rate enhancement by 4×10^{-4} M $[CO_2]$ is less than 10%.
Because the usual concentration of CO_2 from the atmosphere in water at
298 K is ca. 10^{-4} M[123], and experiments in the present work were performed
at higher temperatures, the effect on the reaction rates reported here
should be negligible. Phatak et al[124] have recently reported the
acceleration of the rate of complexation of Cr(III) by EDTA in the
presence of carbonate, nitrite and sulphite ions. The authors explain
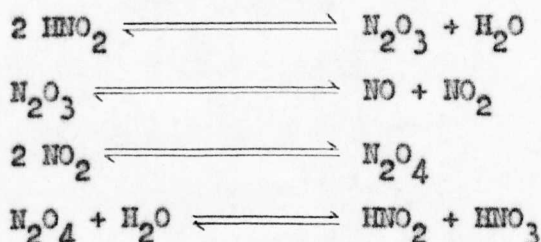
the catalytic effect of these ions by a mechanism involving the assisted deprotonation of a partially co-ordinated intermediate, thus aiding EDTA ring closure. Since all three catalysts are able to co-ordinate with aquochromium(III) complexes without Cr-O bond cleavage[88,121-2], it could be that transient catalyst-chromium(III) complexes are involved in this process.

4.2. The Kinetics of the Nitrous Acid Catalysed Aquation
of Bromopenta-aquochromium(III) Ion

(a) Experimental

The sulphate salt of the complex ion was prepared by a published method[125]. (Found : Cr, 15.7% ; Br, 23.2% ; SO_4^{2-}, 28.6%. Calc. for $[Cr(H_2O)_5Br]SO_4.H_2O$: Cr, 15.5% ; Br, 23.8% ; SO_4^{2-}, 28.6%). Solutions of the complex ion in ca. 1M $HClO_4$, free from sulphate ion, were prepared as required by an ion-exchange technique and stored in the dark, frozen in dry ice. The parameters of the visible spectra of the solutions agreed accurately with those published[125].

Solutions of nitrous acid are known to be unstable[126] and steps were taken to minimise this complication during the kinetic studies. The decomposition occurs by the following set of reactions[126]:

$$2 \ HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

$$N_2O_3 \rightleftharpoons NO + NO_2$$

$$2 \ NO_2 \rightleftharpoons N_2O_4$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_2 + HNO_3$$

The overall stoicheiometry is thus :

$$3 \ HNO_2 \rightleftharpoons 2 \ NO + HNO_3 + H_2O$$
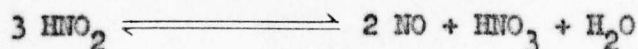
Irreversible loss of HNO_2 ensues if NO and NO_2 are allowed to escape from the solution. This was prevented in the current work by covering the surface of the solutions with liquid paraffin (IR spec. grade) during reactions, a procedure which has been used previously[127] with success, together with the use of tightly stoppered spectrophotometry cells. Gas bubbles were not evident during the experiments. It can be seen from the above equilibria that nitrate ion will inhibit the dissociation of nitrous acid, so a small amount (0.05M) was used in all runs. The extent of the dissociation of HNO_2 under the conditions employed in the aquation studies was assessed by a series of trial experiments. The decay of either the 371 nm or 385 nm absorption peaks

of the nitrous acid spectrum was taken as a measure of the dissociation.
Establishment of the above equilibria was found to be much more rapid
than the rate of aquation of $Cr(H_2O)_5Br^{2+}$ under the same conditions.
However, once equilibrium was reached, the subsequent decomposition was
exceedingly slow, demonstrating that loss of NO and NO_2 from the solutions
had been almost completely prevented. The extent of dissociation of
HNO_2 depended on $[H^+]$ and $[HNO_2]$, as expected from the above set of
equations, and ranged from <1% at 0.8M $[H^+]$ and 0.04M $[HNO_2]$ to 9% at
0.03M $[H^+]$ and 0.005M $[HNO_2]$. Comparative experiments in the absence
of liquid paraffin and nitrate ion showed considerable decomposition.

The kinetics of aquation of the complex were studied spectro-
photometrically at 318.1 K. Nitrous acid solutions were generated
in situ by adding a neutral nitrite solution to an acidic complex
solution in a spectrophotometry cell, the mixture being immediately
covered with liquid paraffin and the cell tightly stoppered. The
faster reactions were followed at a fixed wavelength of 285 nm, while
the slower ones were scanned in the visible region. 285 nm is an
absorption minimum for nitrous acid (E_M ca. 3), while both NO_3^-
(E_M ca. 5) and the product $Cr(H_2O)_6^{3+}$ (E_M ca. 2) have small absorptions,
in addition to that of $Cr(H_2O)_5Br^{2+}$ (E_M ca. 350). A complex concentration
of ca. 10^{-3}M was used for the runs at fixed wavelength. Spectra
scanned in the visible region showed the cleanness of the reaction, the
same isosbestic points (406, 504, and 576 nm) being exhibited both in
the presence and absence of HNO_2. Spectral scans for a typical run
are shown in Figure A of Appendix 1. Kinetic calculations were made
using absorbance data at 640 nm. A complex concentration of ca.
2×10^{-2}M was found to be convenient for experiments carried out in the
visible region. The spectrum at infinite time corresponded to that of
$Cr(H_2O)_6^{3+}$ [128] in all experiments and no spectral evidence for the

presence of intermediates was observed. Free $[H^+]$ and $[HNO_2]$ values in the reaction solutions were calculated from the actual amounts of $HClO_4$ and $NaNO_2$ added using a pK_a value for nitrous acid derived for the temperature employed in the experiments by extrapolating the known[114] pK_a of HNO_2 at 298.1 K and I = 1.0 ($NaClO_4$), using the published[16] enthalpy for the equilibrium.

The uncatalysed aquation reaction has been the subject of previous studies[34,129]. The work was repeated at 318.1 K since the background conditions used were somewhat different to those of the earlier work. Guthrie and King[34] employed $LiClO_4$ to adjust the ionic strength to 1.0, and Zn^{2+} ions were also present in their reaction mixtures. Zinc ions were absent in the present study, while $NaClO_4$ + $NaNO_3$ was used as the backing electrolyte.

(b)   Results

All runs obeyed first-order kinetics to >90% of reaction. Observed rate constants (the means of 2-4 determinations) are presented in Table 4. The same rate law as that previously reported[34,129] was found for the reaction in the absence of nitrous acid :

$$-d[Cr(H_2O)_5Br^{2+}]/dt = (k_o + k_i/[H^+])[Cr(H_2O)_5Br^{2+}]$$

Weighted linear least squares analysis of the data using computer program R002/01 (Appendix 2) gave the following values :

$$10^5 k_o = 6.33 \pm 0.09 \text{ s}^{-1} ; 10^5 k_i = 2.26 \pm 0.03 \text{ M s}^{-1}$$

These results can be compared with those of Guthrie and King[34] at 318.1 K :

$$10^5 k_o = 5.7 \text{ s}^{-1} ; 10^5 k_i = 1.77 \text{ M s}^{-1}$$

The agreement is very good considering the differing background conditions. The behaviour of k_{obs} relative to the reciprocal of the acid concentration is illustrated for both studies in Figure 16.

In the presence of nitrous acid, the aquation rate is dramatically

TABLE 4

Observed Rate Constants for the Aquation
of $Cr(H_2O)_5Br^{2+}$ Catalysed by Nitrous Acid

T = 318.1 K   I = 1.0 ($NaClO_4$ + 0.05M $NaNO_3$)

$[H^+]^a$ M	$[HNO_2]^a$ M	$10^4 k_{obs} (s^{-1})$	E.S.D
0.031	–	7.97	0.11
"	0.005	35.4	0.9
"	0.010	64.4	1.2
"	0.020	113	1
"	0.040	219	1
0.050	–	5.25	0.10
"	0.005	26.3	0.8
"	0.010	47.1	1.0
"	0.020	87.3	2.0
"	0.040	177	4
0.100	–	2.79	0.11
"	0.005	15.1	0.2
"	0.010	29.0	0.6
"	"	31.2[b]	0.1
"	"	33.8[c]	0.5
"	0.020	55.4	1.3
"	0.040	106	3
0.300	–	1.38	0.01
"	0.005	6.03	0.20
"	0.010	10.9	0.3
"	0.020	21.8	0.3
"	0.040	41.3	0.5

$[H^+]^a$ M	$[HNO_2]^a$ M	$10^4 k_{obs}$ (s^{-1})	E.S.D
0.800	–	0.923	0.010
"	0.005	2.59	0.02
"	0.010	4.66	0.03
"	0.020	7.52	0.20
"	0.040	13.4	0.4

(a) Free concentrations in solution, calculated as described in the text.

(b) $[Br^-]$ at 0.02M present.

(c) $[Br^-]$ at 0.20M present.

Other experimental details are outlined in the text.

FIGURE 16

Kinetics of the aquation of the
bromopenta-aquochromium(III) ion
at 318.1 K and I = 1.0
(nitrous acid absent)

A   This work

B   Data from reference 34.

increased. At fixed $[H^+]$ the reaction is first-order in $[HNO_2]$, as shown in Figure 17, and the following rate law is obeyed :

$$-d[Cr(H_2O)_5Br^{2+}]/dt = (k_{H_2O} + k_{HNO_2}[HNO_2])[Cr(H_2O)_5Br^{2+}]$$

where $k_{H_2O} = k_o + k_1/[H^+]$, as defined previously.

The following values of k_{HNO_2} were calculated by a weighted least-squares analysis of the data at each acidity :

$[H^+]/M$	$10^2 k_{HNO_2} (M^{-1} s^{-1})$
0.031	52.9 ± 0.4
0.05	42.0 ± 0.4
0.10	25.5 ± 0.5
0.30	9.99 ± 0.14
0.80	3.56 ± 0.14

Figure 18 shows that the behaviour of k_{HNO_2} with respect to $[H^+]$ is complex. k_{HNO_2} is inverse-acid dependent at high acidities, tending to a zero value at infinite $[H^+]$, but seems to approach a limiting value as the acid concentration decreases. Since an intermediate nitrito-complex is thought to be involved in the catalysis, the fact that the rate law is first-order in $[HNO_2]$ would appear to indicate that a nitrosating agent such as $H_2NO_2^+$ is involved at high acidities[130], rather than N_2O_3 as postulated by Basolo and Hammaker at ca. pH 4. The participation of N_2O_3 would require a second-order term in $[HNO_2]$. The following mechanism for the catalysed pathway is the most simple consistent with the observed data :

$$Cr(H_2O)_5Br^{2+} \xrightarrow[\text{H}_2\text{NO}_2^+]{k_1} Cr(H_2O)_4(ONO)Br \xrightarrow{k_3} \text{products}$$
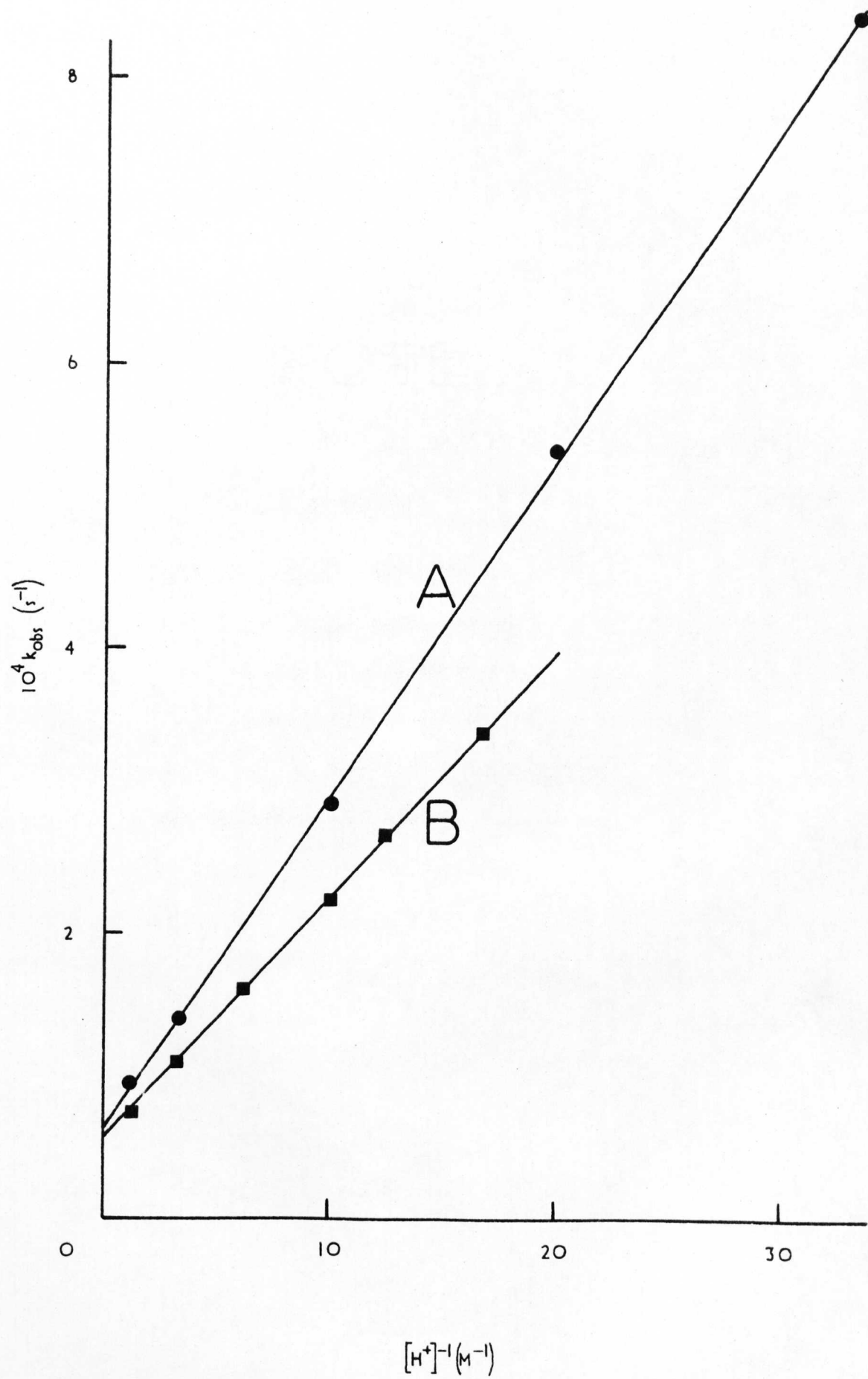
4(i)

FIGURE 17

Kinetics of the aquation of the
bromopenta-aquochromium(III) ion
catalysed by nitrous acid
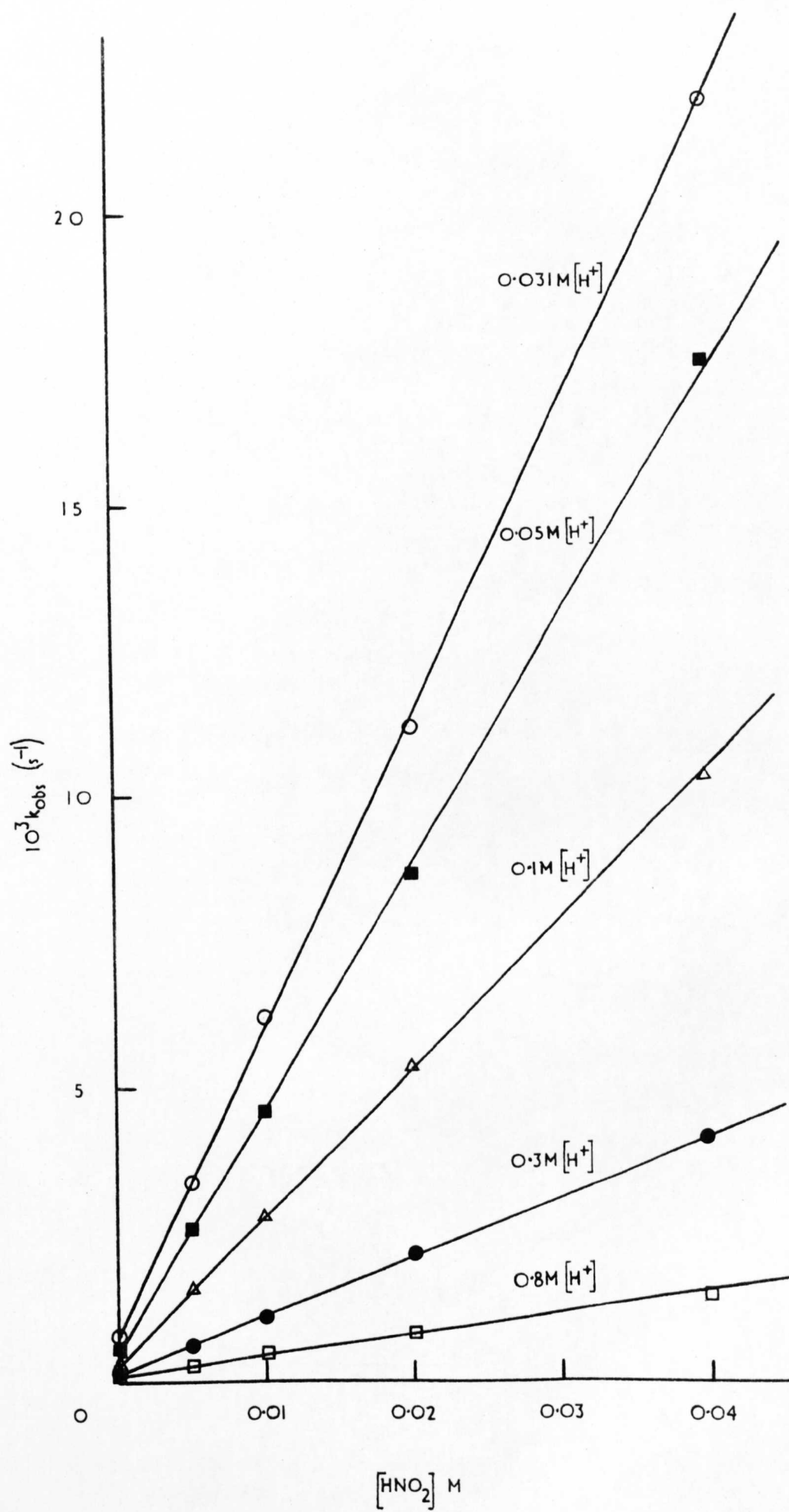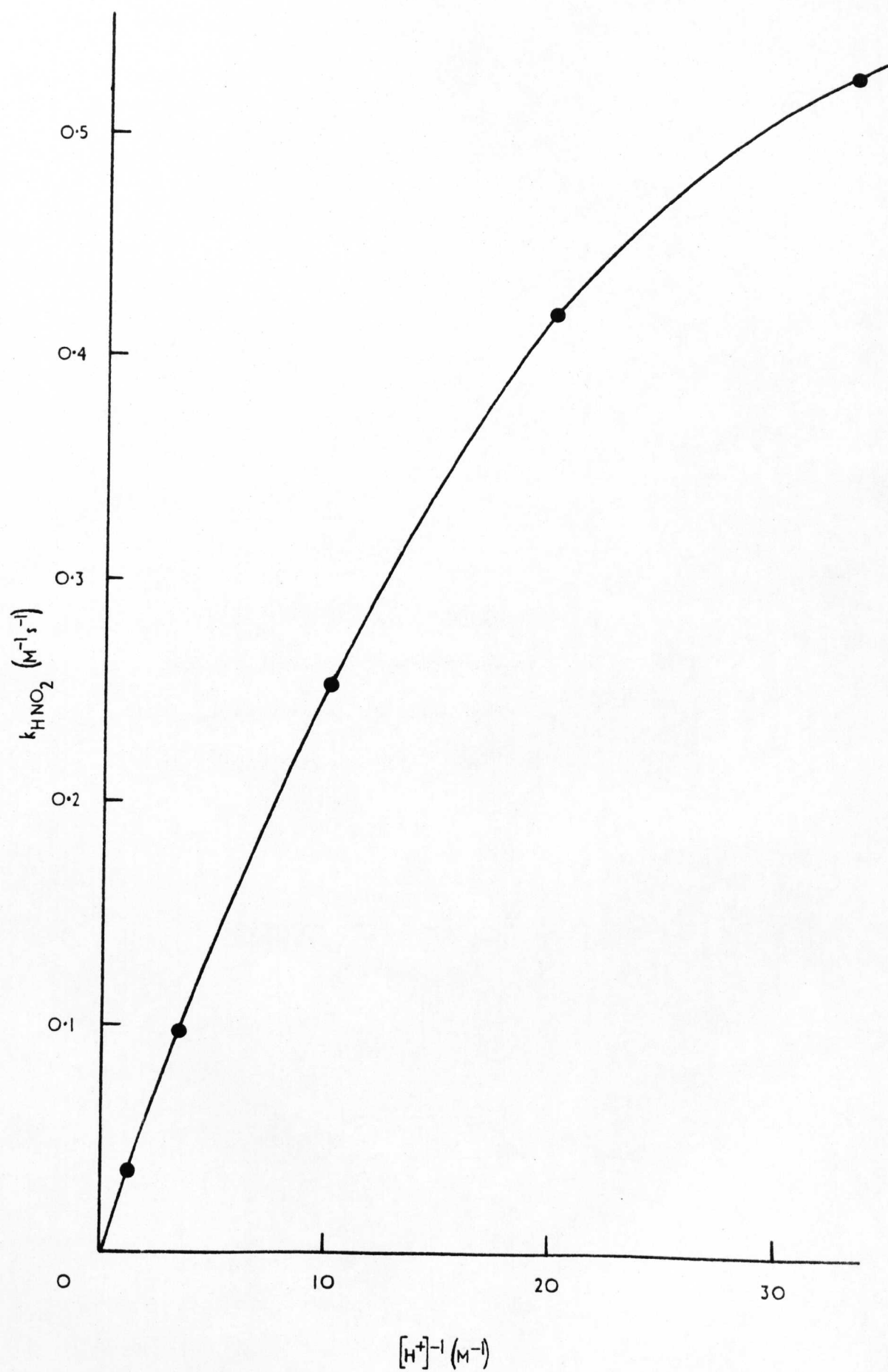at 318.1 K and I = 1.0 ($NaClO_4$).

FIGURE 18

Kinetics of the aquation of the
bromopenta-aquochromium(III) ion
catalysed by nitrous acid
at 318.1 K and I = 1.0 (NaClO$_4$).

Justification for the two reverse steps, k_{-1} and k_{-2}, will be presented in Chapter 5, while the single product step, k_3, will be discussed later in this chapter. Defining $[H_2NO_2^+] = K_1[H^+][HNO_2]$, and applying the steady state approximation to $Cr(H_2O)_4(ONO)Br^+$, the following expression for k_{HNO_2} can be obtained :

$$k_{HNO_2} = k_3k_1K_1[H^+]/(k_3 + k_{-1}[H^+] + k_{-2}[H^+]^2)$$

Investigations reported in Chapter 5 show that the acid hydrolyses of nitritochromium(III) complexes are very rapid at the high acid concentrations and temperature used in this study, hence a valid approximation would seem to be that $k_{-1}[H^+] + k_{-2}[H^+]^2 \gg k_3$. The expression for k_{HNO_2} now reduces to :

$$k_{HNO_2} = k_3k_1K_1/(k_{-1} + k_{-2}[H^+]) \qquad\qquad \text{———} \quad 4(ii)$$

At high acidity, $k_{-2}[H^+] \gg k_{-1}$, so that $k_{HNO_2} = k_3k_1K_1/k_{-2}[H^+]$, demonstrating the inverse-acid dependence and zero k_{HNO_2} intercept shown in Figure 18. At low acid concentration $k_{-1} \gg k_{-2}[H^+]$, so that the limiting rate inferred from Figure 18 is $k_{HNO_2} = k_3k_1K_1/k_{-1}$. By inverting 4(ii) the following expression is obtained :

$$k_{HNO_2}^{-1} = (k_{-1} + k_{-2}[H^+])/k_3k_1K_1$$

The linear relationship of $k_{HNO_2}^{-1}/[H^+]$ is demonstrated in Figure 19. Weighted least-squares analysis of the data gives the line of best fit shown in the figure, and the following values :

$$k_{-1}/k_3k_1K_1 = 0.94 \pm 0.04 \text{ M s}$$

$$k_{-2}/k_3k_1K_1 = 30.0 \pm 0.9 \text{ s}$$

The ratio of the rate constants for the reverse reactions in 4(i),

$$k_{-2}/k_{-1}, \text{ is thus } 32.$$

Considering the outlined mechanism 4(i) and the expression determined for k_{HNO_2}, 4(ii), it is apparent that the term in 4(ii), $k_1K_1/(k_{-1} + k_{-2}[H^+])$, is the effective formation constant, K_1, for the intermediate $Cr(H_2O)_4(ONO)Br^+$.

Kinetics of the aquation of the

bromopenta-aquochromium(III) ion

catalysed by nitrous acid

at 318.1 K and I = 1.0 ($NaClO_4$)
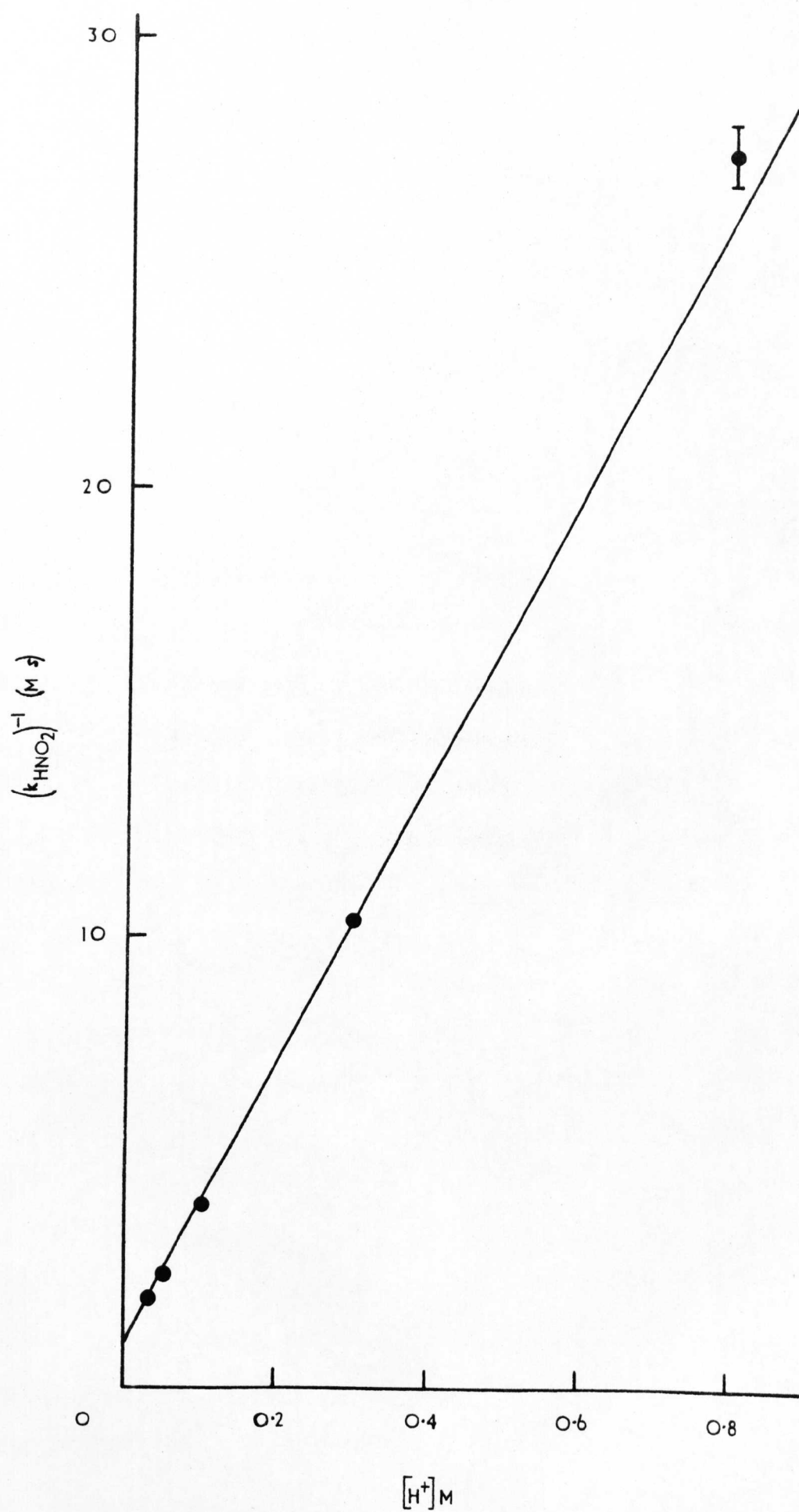
$$K_1 = [Cr(H_2O)_4(ONO)Br^+]/[Cr(H_2O)_5Br^{2+}][HNO_2]$$

Under the most favourable conditions for formation of the intermediate, i.e. low acidity (0.031M $[H^+]$) and high $[HNO_2]$ (0.04M), no evidence for an intermediate could be found spectrophotometrically. Assuming that up to 5% of $Cr(H_2O)_5Br^{2+}$ could exist as the intermediate without being detected, a maximum value for K_1 of 1.35M^{-1} can be determined. Now, since $k_{HNO_2} = 0.529$ M^{-1} s^{-1} at 0.031M $[H^+]$ and $k_{HNO_2} = K_1 k_3$, a value of $k_3 > 0.4$ s^{-1} is inferred.

If it is assumed that the decrease in charge is the only factor which renders loss of Br$^-$ from the intermediate faster than from $Cr(H_2O)_5Br^{2+}$, it is possible to estimate a value of k_3. The rate of loss of bromide ion from $Cr(H_2O)_4(ONO)Br^+$ should be very similar to that from $Cr(H_2O)_4Br_2^+$. Holba and co-workers[129] quote an acid-independent rate constant for the aquation of $Cr(H_2O)_4Br_2^+$ of 2.7 X 10^{-4} s^{-1} at 298.1 K. The fact that the isomeric form of the complex studied by Holba[129] was not stated, and that it is not known which form the postulated intermediate, $Cr(H_2O)_4(ONO)Br^+$, possesses is probably not important, since the reported[131] acid-independent rate constants for the aquation of cis- and trans-$Cr(H_2O)_4Cl_2^+$ differ by less than a factor of two at 298.1 K. The activation energy associated with the aquation of $Cr(H_2O)_4Br_2^+$ has not been measured, but a value can be estimated from the aquation reactions of similar systems: The activation energy of the acid-independent rate constant for the aquation of $Cr(H_2O)_5Br^{2+}$ is only 0.5 kcal. mol^{-1} less than that of $Cr(H_2O)_5Cl^{2+}$. Johnson and Reynolds[131] quote an E_a value of 26.5 kcal. mol^{-1} for the aquation of trans-$Cr(H_2O)_4Cl_2^+$ at 1.0M $[H^+]$, where contribution from the rate term dependent on inverse-acid concentration is negligible[132]. Hence, assuming that the activation energy for the acid hydrolysis of $Cr(H_2O)_4Br_2^+$ is ca. 26 kcal. mol^{-1}, a value for the acid-independent rate constant

of 0.02 s^{-1} can be calculated at 318.1 K. That this calculated value is a factor of 20 times less than the minimum value of k_3 deduced from the **experimental results** appears to indicate that factors other than a lower charge may be important in conferring increased lability on the $Cr(H_2O)_4(ONO)Br^+$ intermediate.

The observed data appear to fit the proposed mechanism, 4(i), satisfactorily in the pH range studied. It is possible that at higher pH values a more complicated mechanism could ensue due to the participation of species such as N_2O_3 and $Cr(H_2O)_4(OH)Br^+$. The very small rate enhancement observed for the catalysed aquation reaction in the presence of excess bromide ion (see Table 4), demonstrates that HOBr is probably no more efficient at forming the nitrito-intermediate than is $H_2NO_2^+$. The **slight rate** acceleration observed could simply be due to a medium effect caused by the exchange of ClO_4^- for Br^-.

4.3.   The Effect of Nitrous Acid on the

Aquations of Chloropenta-aquochromium(III)

and Bromopenta-aminechromium(III) Ions

(a)   Experimental

The sulphate salt of the $Cr(H_2O)_5Cl^{2+}$ ion and the bromide of $Cr(NH_3)_5Br^{2+}$ were prepared by published methods[133-4]. The samples were not analysed chemically, but the visible spectra obtained in dilute perchloric acid agreed excellently with those reported[125,135]. ($Cr(H_2O)_5Cl^{2+}$, found : λ_{max} 428 nm (E_M 21.9) ; λ_{max} 609 nm (E_M 17.4). Reported : λ_{max} 428 nm (E_M 21.9) ; λ_{max} 608 nm (E_M 17.4). $Cr(NH_3)_5Br^{2+}$, found : λ_{max} 379 nm (E_M 41.0) ; λ_{max} 468 nm (E_M 24.5) ; λ_{max} 523 nm (E_M 38.9). Reported : λ_{max} 378 nm (E_M 41) ; λ_{max} 468 nm (E_M 25) ; λ_{max} 523 nm (E_M 38)).

The aquations of both complexes were studied spectrophotometrically in the visible region in the presence of HNO_2, spectra being scanned as the reactions proceeded. In both cases isosbestic points were observed which were identical to those of the uncatalysed reactions (for $Cr(H_2O)_5Cl^{2+}$ at 406, 498, and 578 nm, and for $Cr(NH_3)_5Br^{2+}$ at 427 and 498 nm). No evidence for intermediates was observed and the spectra of the final products agreed accurately with those of $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_5H_2O^{3+}$. Good first-order rate plots were obtained to > 90% of reaction for both complex ions. $Cr(NH_3)_5Br^{2+}$ was added to the reaction mixture directly as the solid bromide salt. Acidic solutions of $[Cr(H_2O)_5Cl]SO_4.H_2O$ were prepared and sulphate removed by the addition of a stoicheiometric quantity of $Ba(ClO_4)_2$ solution, the $BaSO_4$ precipitate being separated by centrifuging. Other experimental details were as described in Section 4.2(a).

(b)   Results

The observed rate constants obtained in these experiments and the literature values for the aquations are presented in Table 5 :

TABLE 5

Complex Ion	$[HNO_2]$/M	$[H^+]$/M	Temperature (K)	$10^5 k_{obs}$ (s^{-1})
$Cr(H_2O)_5Cl^{2+}$ [a]	–	0.032	323.1	5.1
$Cr(H_2O)_5Cl^{2+}$ [b]	0.01	0.032	"	55 ± 1
$Cr(NH_3)_5Br^{2+}$ [c]	–	0.10	298.4	8.6
$Cr(NH_3)_5Br^{2+}$ [b]	0.05	0.45	"	9.0 ± 0.5

(a) Ref. 38, ionic strength adjusted to 1.0 with $LiClO_4$.

(b) This work. $[H^+]$ and $[HNO_2]$ are the free concentrations existing in the solutions, calculated as described in Section 4.2(a).

(c) Ref. 115. The value of k_{obs} was obtained for I = 1.0 ($NaClO_4$) by extrapolating the value at I = 0.1 using the ionic strength dependence reported. The rate of aquation of the penta-ammine complex is not expected[1c] to be pH dependent in this range of acidity.

The acceleration of the aquation rate of the chloropenta-aquochromium(III) ion by a factor of ca. 10 in the presence of 0.01M $[HNO_2]$ is similar to that observed under similar conditions for $Cr(H_2O)_5Br^{2+}$. However, to within the limits of experimental error, the aquation rate of $Cr(NH_3)_5Br^{2+}$ is unaffected by the presence of HNO_2, under conditions such that the rate of aquation of $Cr(H_2O)_5Br^{2+}$ should be enhanced at least 20 times. These results would appear to demonstrate that the catalysis is a general effect for halopenta-aquochromium(III) ions and possible other halo-aquochromium(III) complexes. Since it seems that the presence of water molecules in the complex is necessary for catalysis to occur, the postulate of the participation of a nitrito- intermediate would appear to be eminently reasonable. This conclusion is further supported by the studies on cis- and trans-$Cr(H_2O)_4Cl_2^+$ and cis- and trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$ described later.

In view of the efficient catalytic activity of HNO_2 on the aquation

reactions of halopenta-aquochromium(III) ions, other oxyacids were
investigated under similar conditions, to see if the effect is specific
for nitrous acid.   The results are presented in the next section.

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investigated under similar conditions, to see if the effect is specific
for nitrous acid.   The results are presented in the next section.

4.4. Attempted Catalysis of the Aquations of

Halopenta-aquochromium(III) Complexes

using other Oxyacids

(a) Experimental

For convenience, solid $[Cr(H_2O)_5X]SO_4.H_2O$ was added to thermostatted reagent solutions. Since acceleration of the aquation reactions of complex ions has been reported[115] due to ion-pairing with sulphate ion, some kinetic determinations were carried out in the absence of added oxyacids to ensure that a valid comparison rate of aquation was available. The oxyacids were added to reagent solutions as their sodium salts, except for KIO_3, and CH_3COOH, H_3BO_3, and H_3PO_3 used in the acid form. The materials were A.R. grade or recrystallised G.P.R. Other experimental details were as described in Section 4.2(a).

All the reaction rates were first-order in complex concentration to at least 75% completion and exhibited the isosbestic points noted previously. In all but two cases the product appeared to be solely $Cr(H_2O)_6^{3+}$. With $(COOH)_2$ and HIO_3, however, deviations from a clean reaction became apparent after some time. Both acids are known to complex with $Cr(H_2O)_6^{3+}$ in acidic solution[136-7]. Absorbance readings at infinite time were estimated by Swinbourne's method[96], using computer program R001/08 (Appendix 2) for these two cases. HIO_3 could not be used in conjunction with $Cr(H_2O)_5Br^{2+}$ since the released Br^- was oxidised to bromine.

(b) Results

The observed rate constants for the various oxyacids used are presented in Table 6 :

TABLE 6

$T = 318.1$ K, $I = 1.0$ ($NaClO_4$), $[Oxyacid] = 0.01M$ (total concentration added)

Complex Ion	Oxyacid	$[H^+]M$	$10^4 k_{obs}(s^{-1})$
$Cr(H_2O)_5Br^{2+}$	--	0.10	3.1
"	CH_3COOH	"	3.4
"	H_3BO_3	"	3.2
"	H_2SO_3	"	3.2
"	H_2CO_3	"	3.2
"	H_3PO_2	"	3.3
"	H_3PO_3	"	3.2
"	$(COOH)_2$	"	3.2
"	HCNO	"	3.4
"	HCNO[a]	"	4.6
$Cr(H_2O)_5Cl^{2+}$	-	0.01	1.23
"	HIO_3	"	1.45

(a) $[Oxyacid] = 0.04M$

To within experimental error, the rates of aquation were affected by added oxyacids in only two instances, that of HIO_3 and the higher concentration of HCNO. Since the experiment in the presence of iodic acid was complicated by complex formation with the product $Cr(H_2O)_6^{3+}$, the rate constant obtained probably has a large associated error and the ca. 18% rate enhancement may not be significant. The ca. 50% acceleration of the aquation of $Cr(H_2O)_5Br^{2+}$ in the presence of 0.04M cyanic acid is interesting, and possibly indicates the same effect as that exhibited by nitrous acid. Ion-pair formation is unlikely to account for the rate enhancement, since simple monovalent ions do not normally exhibit such a marked effect, and, at the acidity employed, very little CNO^- would be present anyway. However, nitrous acid under

similar conditions demonstrates a ca. 4000% rate acceleration, so is far more active than cyanic acid, if the catalytic processes are similar.

It was mentioned earlier that the lability of the proposed intermediate, $Cr(H_2O)_4(ONO)Br^+$, with respect to loss of Br^-, does not appear to be due solely to its single positive charge. The iodo-ligand in $Cr(H_2O)_5I^{2+}$ is able to labilise a co-ordinate water molecule by a presumed _trans_ effect[61], as discussed in Chapter 3. It might be that a nitrito-group can exercise a similar effect, and this possibility is investigated in the next section.

4.5.   The Nitrous Acid Catalysed Aquations of cis-
        and trans-Dichlorotetra-aquochromium(III) Ions

(a)   Experimental

Commercially available A.R. "Chromic Chloride" is known[138] to be
pure trans-$[Cr(H_2O)_4Cl_2]Cl$, so this salt was used without further
purification as a source of the trans isomer.   Solutions of cis-
$Cr(H_2O)_4Cl_2^+$ in ca. 0.4M HClO$_4$ were prepared by a published method[139].
The aquation rates of the two complex ions were determined spectro-
photometrically at 720 nm, an isosbestic point for the two isomers[138],
in order to avoid any spectral complication caused by the isomerization
reaction.   Due to the subsequent hydrolysis of the primary product,
$Cr(H_2O)_5Cl^{2+}$, infinity readings were calculated using the method of
Swinbourne[96].   Other experimental details have been outlined in
Section 4.2(a).

(b)   Results

The kinetic results are collated in Table 7 :

TABLE 7

T = 307.9 K,   [Complex] ca. 0.03M

[H$^+$]/M	[HNO$_2$]/M	$10^4 k_{obs}$ (s^{-1})	
		cis-	trans-
0.054	–	1.4	2.5
"	0.01	5.6	6.7
"	0.02	7.2	8.3
0.203	–	0.8	1.9
"	0.01	1.9	3.0
"	0.02	3.1	4.3
"	0.03	3.9	–

Salzmann and King[139] studied the aquation reactions in the absence of nitrous acid at $[H^+] = 0.203M$ and $T = 307.9$ K. They report an aquation rate for the cis-isomer of 0.83×10^{-4} s^{-1} and for the trans- of 1.8×10^{-4} s^{-1}, in good agreement with this study. Because the aquation reactions of both isomers are catalysed by nitrous acid it would appear that a trans-effect is not responsible for the catalysis, and that either a cis-effect[1c] is operating or the relative positions of the nitrito and leaving groups in the intermediate are unimportant. However, it is impossible to be dogmatic about this conclusion since Salzmann and King[139] have demonstrated that an apparently intramolecular isomerization occurs between the two isomeric $Cr(H_2O)_4Cl_2^+$ species, at a rate approaching that of aquation. Though the isomerization reaction alone does not necessarily invalidate the results in the presence of HNO_2, it might be possible for nitrous acid to have an accelerating effect on the isomerization as well as the aquation reactions, in which case the results would be inconclusive.

The isomers cis- and trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$ are known to aquate with better than 90% retention of configuration, and interconversion of the two isomeric chloro-complexes does not appear to be a problem[140]. This system also possesses the advantage that the three mechanistic possibilities of a cis-, trans-, or ambi-positional effect can be determined. The results of the study are presented in the next section.

4.6. The Effect of Nitrous Acid on the Aquations of the cis-
and trans-Chloro-aquotetra-amminechromium(III) Ions

(a) Experimental

The complexes cis- and trans-$[Cr(NH_3)_4(H_2O)Cl]Cl_2$ were prepared by the methods of Hoppenjans and Hunt[141]. Analysis of the compounds gave excellent results (Found for cis isomer : Cr, 21.4% ; N, 22.8% ; Cl, 43.4%. Found for trans isomer : Cr, 21.5% ; N, 22.8% ; Cl, 43.2%. Calc. for $[Cr(NH_3)_4(H_2O)Cl]Cl_2$: Cr, 21.3% ; N, 22.9% ; Cl, 43.4%). The chloride salts were converted into perchlorates as described by Hoppenjans and Hunt[141] for use in the kinetic experiments, which were carried out spectrophotometrically at 303.1 K, employing the methods described in Section 4.2(a). Kinetic runs followed by scanning spectra exhibited the same isosbestic points in both the presence and absence of nitrous acid. Observed for the aquation of the cis-isomer : 432 nm (E_M 10), 501 nm (E_M 36), theoretical for the reaction

$$\text{cis-}Cr(NH_3)_4(H_2O)Cl^{2+} \longrightarrow \text{cis-}Cr(NH_3)_4(H_2O)_2^{3+} : 432 \text{ nm } (E_M \text{ 10}),$$

501 nm (E_M 35). Observed for the aquation of the trans-isomer : 436 nm (E_M 14), ca. 530-5 nm (E_M 17) ; theoretical for the reaction

$$\text{trans-}Cr(NH_3)_4(H_2O)Cl^{2+} \longrightarrow \text{trans-}Cr(NH_3)_4(H_2O)_2^{3+} : 430 \text{ nm } (E_M \text{ 14}),$$

534 nm (E_M 17). In the presence of nitrous acid these isosbestic points were no longer maintained after ca. 65% reaction for the cis- and ca. 50% for the trans-isomer. Jorgenson and Bjerrum[142] have shown that at 313 K and 0.1 M $[H^+]$ trans-$Cr(NH_3)_4(H_2O)_2^{3+}$ loses ammonia at an observed rate of ca. $3 \times 10^{-4} s^{-1}$ and that the rate for the cis-isomer is ca. $3 \times 10^{-5} s^{-1}$. Even allowing a factor of ten decrease in these rates at the lower temperature used in this study, it is obvious that the subsequent reactions of the products will have an effect on the spectra obtained during the kinetic investigations of the aquation reactions of the chloro-aquotetra-amminechromium(III) complexes. Hoppenjans et al[140] presumably discovered this complication also in the

measurements of the uncatalysed aquation rates, since Guggenheim's method[28d] was used to calculate rate constants. It is interesting that the subsequent reactions of the di-aquo-products appear to be more marked in the presence of nitrous acid, and this may indicate that HNO_2 has a slight catalytic effect on the dissociation of NH_3 from aquo-amminechromium(III) complexes.

Rate constants were calculated only from data obtained in the early course of the reactions, where the isosbestic points were known to hold. Since long extrapolations were involved, Swinbourne's method[96] for estimating infinity readings was unreliable. Instead, absorbances at infinite time were calculated assuming that the final product was pure cis- or trans-di-aquo complex as appropriate. Spectral scans up to 65% completion for a typical run involving cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ in the presence of HNO_2 are shown in Figure B of Appendix 1.

(b) Results

The observed rate constants for the aquations of both cis- and trans-chloro-aquotetra-amminechromium(III) ions are shown in Table 8 :

TABLE 8

$T = 303.1$ K, $I = 1.0$ (NaClO$_4$), $[NO_3^-] = 0.05$M, $[Complex]$ ca. 10^{-2}M

		$10^6 k_{obs} (s^{-1})$	
$[H^+]^a$M	$[HNO_2]^a$M	cis-	trans-
0.031	–	14[b]	3.9[c]
"	0.01	75[e]	4.0
"	0.02	140[e]	4.2
"	0.04	270[b]	4.4[d]
0.10	–	12[g]	3.0[h]
"	0.02	140[e]	3.2
"	0.04	280[f]	–

(a) Free concentrations in solution.

(b) Spectra scanned using Cary 14.   Data at 550 nm.

(c) As (b) but data at 390 nm. [Complex] ca. 2 X 10^{-2} M.

(d) As (c) but data at 580 nm.

(e) Fixed wavelength of 600 nm using Cary 14 with 0-0.2 absorbance slidewire.

(f) Fixed wavelength of 550 nm on Cary 14. [Complex] ca. 2 X 10^{-2} M.

(g) From the work of Hoppenjans et al[140], extrapolated to 303.1 K, k_{obs} = 13 X 10^{-6} s^{-1}.

(h) As (g) but for trans-complex, k_{obs} = 2.5 X 10^{-6} s^{-1}.

In the absence of any qualification, the kinetic runs were carried out at a fixed wavelength of 600 nm using the Gilford recorder.

It is obvious from Table 8 that the aquation of cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ is markedly catalysed by HNO_2, while the reaction of the trans-isomer is almost unaffected.   The difference in behaviour of the two isomeric complexes is well illustrated by a comparison of the rate plots obtained in the absence and presence of 0.04 M $[HNO_2]$ at $[H^+]$ = 0.031 M, shown in Figure 20.   The extent of the acceleration for the cis-isomer is of the same order as that observed for the aquations of $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_5Br^{2+}$, and since the catalytic mechanism should certainly be the same as that postulated for $Cr(H_2O)_5Br^{2+}$, it is worthwhile to compare the two sets of results. k_{HNO_2} values (as defined in Section 4.2(b)) for the aquation of cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ are approximately the same at the two acidities studied (k_{HNO_2} = 6.5 X $10^{-3}M^{-1}s^{-1}$ at 0.1 M $[H^+]$, and 6.3 X $10^{-3}M^{-1}s^{-1}$ at 0.031 M $[H^+]$, while k_{HNO_2} values for $Cr(H_2O)_5Br^{2+}$ at the same two acid concentrations differ from one another (k_{HNO_2} = 0.26 and 0.53 $M^{-1}s^{-1}$).   This would appear to indicate that the limiting rate of k_{HNO_2} (as explained in Section 4.2(b)) for the catalysed aquation of cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ is maintained to as high an acid concentration as 0.1 M.   This behaviour is not, however, surprising considering the probable relative values of k_{-1} and k_{-2} (as defined

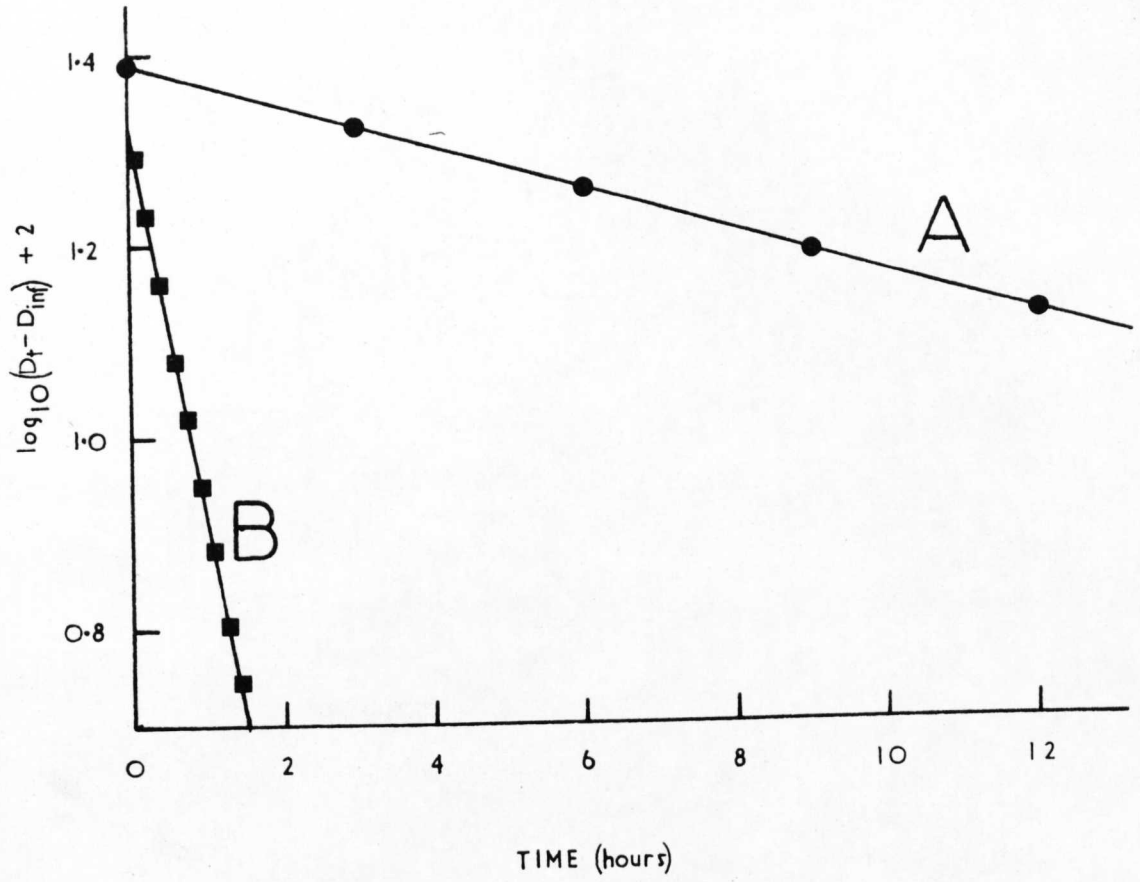Rate plots for the aquation of the

cis- and trans-chloro-aquotetra-amminechromium(III) ions

at 303.1 K, $[H^+]$ = 0.031M, and I = 1.0 ($NaClO_4$)

Upper illustration - cis-isomer

Lower illustration - trans-isomer

    A - nitrous acid absent

    B - $[HNO_2]$ = 0.04M

TIME (hours)

TIME (hours)

in 4(i)). A study of the acid catalysed hydrolysis of trans-$Cr(NH_3)_4(ONO)Cl^+$ is contained in Chapter 5 and the results at 303.1 K show that k_{-1} and k_{-2} are of approximately the same magnitude. The values of k_{-1} and k_{-2} are probably similar for the presumed intermediate cis-$Cr(NH_3)_4(ONO)Cl^+$, so that at 0.1 M $[H^+]$ the term in the rate equation 4(ii), $k_{-2}[H^+]$, would be ca. 10% of k_{-1}. Since the rate data in Table 8 are probably accurate to only ± 10%, because of the complications involved in the experiments, the similarity in the two k_{HNO_2} figures obtained for different acidities for the catalysed aquation of cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ is reasonable.

Two possibilities exist to explain the sensitivity of the cis-isomer to catalysed aquation by nitrous acid. Either the presumed intermediate cis-$Cr(NH_3)_4(ONO)Cl^+$ is formed to a far greater extent than the corresponding trans-complex, or the cis-intermediate is much more labile with respect to loss of halogen. The next section describes various preparative and miscellaneous experiments which tend to support the latter explanation.

4.7.   Preparative and Miscellaneous Experiments

(a)   Attempted Preparation of the Chloronitritotetra-aquochromium(III)

Ion

Spectral examination of the reaction occurring at 273 K and pH 3 of $Cr(H_2O)_5Cl^{2+}$ with a ten-fold concentration of HNO_2/NO_2^- showed a clean reaction with isosbestic points (410, 492, and 583 nm) which were not the same as observed at lower pH values (406, 498, and 578 nm). The product was not $Cr(H_2O)_6^{3+}$, the spectrum having a λ_{max} of 565 nm (E_M ca. 17). Separation of the products, using an ion-exchange technique at 273 K and eluting with $NaClO_4$ solutions at pH 3.7, showed no evidence of a species of charge +1. A 1M $NaClO_4$ solution eluted a violet band, the spectrum of which agreed with that of the $Cr(H_2O)_5ONO^{2+}$ ion (see Chapter 5). A grey-blue band eluted with 4M $NaClO_4$ proved to be the $Cr(H_2O)_6^{3+}$ ion. Thus, at this pH value and a low temperature such that the postulated intermediate $Cr(H_2O)_4(ONO)Cl^+$ is not particularly labile with respect to loss of co-ordinated nitrite, it appears to be just as liable to lose chloride from the inner sphere.

(b)   Preparation of trans-Dinitritotetra-amminechromium(III) perchlorate

Trans-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$ (1g), prepared by the method of Hoppenjans and Hunt[141], was dissolved in water (10 ml) containing 1 drop of glacial acetic acid at room temperature. With vigorous stirring, finely ground sodium nitrite (A.R., 0.8g) was added. On standing the solution for a few minutes, orange crystals began to form. After cooling with ice for several minutes the crystals were filtered off, and washed with ice-cold 50 : 50 ethanol/water, then absolute alcohol, and finally ether. The compound was dried under vacuum over silica gel. Yield 0.5g. (Analysis. Found : Cr, 16.7% ; N, 26.9% ; Cl, 11.4% ; NO_2^-, 28.9%. $[Cr(NH_3)_4(ONO)_2]ClO_4$ requires : Cr, 16.7% ; N, 27.0% ; Cl, 11.4% ; NO_2^-, 29.5%). The visible and near UV spectrum of this complex, which has not been prepared previously, was recorded in water

at ca. 280 K, and is shown in Figure C of Appendix 1. The spectral parameters are as follows : λ_{min} 309 nm (E_M 140), λ_{max} 325 nm (E_M 146), shoulder ca. 335 nm (E_M ca. 140), λ_{min} 422 nm (E_M 11.8), λ_{max} 488 nm (E_M 38.7). Slight structure on the UV absorption band is evident, presumably due to the nitrito-ligands. The complex appears to be reasonably stable in neutral aqueous solution, in the dark. The spectrum changes only slowly at room temperature ; however, after long periods, there is ample evidence for decomposition involving loss of ammonia. Absorption peaks decline in intensity and shift to higher wavelengths. The pH of the solution rises and, eventually, a pale blue gelatinous precipitate develops, indicating the formation of hydroxochromium(III) species. If a fresh solution of the dinitrito-complex is acidified, there is a rapid reaction and the spectrum of the products corresponds to trans-$Cr(NH_3)_4(H_2O)_2^{3+}$ [141] + 2 equivalents of HNO_2. Preliminary investigations[88] of the kinetics of this reaction indicate that the hydrolyses of the first and second nitrito-groups occur at approximately the same rate.

(c)   Preparation of cis-Dinitritotetra-aminochromium(III) Perchlorate

The complex was prepared and dried by the same methods as those employed for the trans-isomer, but using cis-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$ as the starting material, dissolved in 5 ml of water. Yield 0.5g. (Analysis. Found : Cr, 16.9% ; N, 26.9% ; Cl, 11.4% ; NO_2^-, 30.1% . Calc. for $[Cr(NH_3)_4(ONO)_2]ClO_4$: Cr, 16.7% ; N, 27.0% ; Cl, 11.4% ; NO_2^-, 29.5%). The complex is unstable in aqueous solution at all pH values, even in nitrite buffer at ca. pH 4 and 275 K. The spectrum of the compound in neutral aqueous solution at 275 K, illustrated in Figure D of Appendix 1, was estimated by scanning spectra at intervals and extrapolating back to zero time. The spectral parameters obtained were : λ_{max} 362 nm (E_M ca. 121) and λ_{max} 492 nm (E_M ca. 65). The reported[143] parameters are : λ_{max} 361 nm (E_M 126) and λ_{max} 494 nm

(E$_R$ 79). Kyuno et al[143] state that the bromide salt of the complex is
moisture and light sensitive, but do not say how they obtained their
spectrum, except that an aqueous solution at 278 K was used. The
primary decomposition step at neutral pH appears to be loss of one
nitrito-ligand, since after ca. 15 minutes at 275 K the spectrum
corresponds closely to that of cis-Cr(NH$_3$)$_4$(H$_2$O)(ONO)$^{2+}$ (see below).
Further decomposition is much slower and involves loss of ammonia, as
described for the trans-complex. The observation that one nitrito-
ligand of cis-Cr(NH$_3$)$_4$(ONO)$_2^+$ is much more labile than the other, while
the labilities seem to be equal in the trans-isomer, has also been made
with the analogous ethylenediamine complexes[94]. In view of the ease
with which cis-Cr(NH$_3$)$_4$(ONO)$_2^+$ loses one nitrito-ligand, even in the
presence of an excess of nitrite ion, it seems surprising that the complex
ion can be isolated. Trial experiments showed that the low solubility
of the perchlorate salt is probably responsible. The efficacy of ClO$_4^-$
in precipitating complex ions of charge +1 is well known[144]. Acid-
ification of a fresh solution of the cis-dinitrito complex rapidly gives
products with a spectrum corresponding to that of cis-Cr(NH$_3$)$_4$(H$_2$O)$_2^{3+}$[141]
+ 2 equivalents of HNO$_2$. That cis- and trans-Cr(NH$_3$)$_4$(ONO)$_2^+$ have the
configurations assigned is obvious, since no Cr - O bond fission[119]
should occur in their preparations. The spectra of the same isomeric
form of the dinitritotetra-amminechromium(III) and dinitritobisethylene-
diamminechromium(III)[94] complexes compare quite closely.

(d) Preparation of trans-Nitrito-aquotetra-amminechromium(III)
Chloride

Trans-[Cr(NH$_3$)$_4$(ONO)$_2$]ClO$_4$ (0.2g) was dissolved in the minimum
possible volume of ice-cold water, and one equivalent of H$^+$ in the form
of 1M HCl was added dropwise, with stirring. After approximately ten
minutes at 273 K, finely ground MgCl$_2$ (A.R.) was added with stirring
until a pale pinkish-orange precipitate developed. The product was

recrystallised from ice-cold water using a saturated $MgCl_2$ solution, and dried under vacuum over silica gel. Yield 0.05g. (Analysis. Found : Cr, 20.1% ; N, 27.5% ; Cl, 28.4% ; NO_2^-, 18.0%. $[Cr(NH_3)_4(H_2O)(ONO)]Cl_2$ requires : Cr, 20.4% ; N, 27.5% ; Cl, 27.8% ; NO_2^-, 18.1%). The possibility that the substance obtained could have been, fortuitously, a 1 : 1 mixture of the dinitrito and di-aquo complexes was rendered unlikely by a repeat preparation under slightly different conditions, which gave a sample that exhibited an exact 1 : 1 Cr : NO_2^- ratio on analysis. The visible spectrum of the complex, Figure E of Appendix 1, was recorded at 273 K in a pH 4 phthalate buffer solution to avoid any complication due to the formation of a hydroxy-species. The buffer solution was non-absorbing in the wavelength region 300-700 nm, and the constituents appeared not to complex with aquochromium(III) species over a short period of time. The spectral details are : λ_{min} 313 nm (E_M 62), shoulder ca. 327 nm (E_M ca. 65), shoulder ca. 357 nm (E_M ca. 74), λ_{max} 363 nm (E_M 75), λ_{min} 421 nm (E_M 16), λ_{max} 492 nm (E_M 32). Even in the dark, the complex in water slowly decomposes by loss of ammonia, as described in Section 4.7(b). Acidification of a fresh solution rapidly produces species with a spectrum corresponding to trans-$Cr(NH_3)_4(H_2O)_2^{3+}$ + 1 equivalent of HNO_2.

(e) **Preparation of cis-Nitrito-aquotetra-amminechromium(III) Chloride**

The complex was prepared, recrystallised, and dried in a similar manner to that of the trans-isomer described above. However, the addition of acid was not required, the cis-dinitrito-complex was simply allowed to aquate in neutral solution for ca. 15 minutes before the addition of $MgCl_2$. The yield of the preparation was 0.1g, and the product is pale pinkish-orange in colour. A full analysis of the complex was not attempted, but determinations on three separate samples all gave a Cr : NO_2^- ratio of exactly 1 : 1. The visible spectrum of

the complex in water at 273 K (Figure F of Appendix 1) has the following parameters : λ_{min} 317 nm (E_M 69), λ_{max} 364 nm (E_M 94), λ_{min} 422 nm (E_M 21), λ_{max} 491 nm (E_M 54). The decompositions of the complex in neutral and acidic aqueous solutions exhibit similar characteristics to those of the <u>trans</u>-isomer. The author is indebted to Mr. Alan Toft for much of the work on <u>cis</u>-$[Cr(NH_3)_4(H_2O)(ONO)]Cl_2$, performed as part of an undergraduate research project.

(f)   <u>Preparation of trans-Cloronitritotetra-amminechromium(III)</u>
<u>Perchlorate</u>

<u>Trans</u>-$[Cr(NH_3)_4(H_2O)Cl](ClO_4)_2$ (1g) was dissolved at room temp-
erature in water (<u>ca</u>. 20 ml) containing three drops of glacial acetic
acid. The solution was filtered, then finely ground sodium nitrite
(0.8g) was added, with stirring. Precipitation commenced after a few
minutes, and the solution was cooled in ice. The purplish-pink product
was filtered off and washed copiously with methanol, in which the
starting materials are soluble. The solid was dried under vacuum
over silica gel. Yield 0.5g. (Analytical results. Found :
Cr, 17.5% ; N, 23.9% ; Cl, 24.4% ; NO_2^-, 13.8%. $[Cr(NH_3)_4(ONO)Cl]ClO_4$
requires: Cr, 17.3% ; N, 23.3% ; Cl, 23.6% ; NO_2^-, 13.6%). In neutral
aqueous solution the complex is the most stable of all the nitrito-
complexes so far described, very little change occurring in the visible
spectrum during 30 minutes at room temperature. The visible spectrum
in water at 283 K, Figure G of Appendix 1, has these particulars :
shoulder <u>ca</u>. 325 nm (E_M <u>ca</u>. 82), λ_{min} 350 nm (E_M 73.4), λ_{max} 366 nm
(E_M 76.5), λ_{min} 435 nm (E_M 14.2), slight shoulder <u>ca</u>. 475 nm (E_M <u>ca</u>. 21),
λ_{max} 535 nm (E_M 31.6). The complex dissolved in aqueous perchloric
acid gives a spectrum corresponding to that of <u>trans</u>-$Cr(NH_3)_4(H_2O)Cl^{2+}$ [141]
+ 1 equivalent of HNO_2.

The nitrito-complexes prepared in Sections (b) to (f), and, indeed,
all other Cr(III) compounds used in this study, were stored in a dessicator

in darkened bottles. No deterioration of samples was evident for periods of several months when kept in this manner. Infra-red spectral parameters of the nitrito-complexes prepared are listed in Table A of Appendix 1. The evidence that the co-ordinated nitrite ligands are $\underline{O}$- and not $\underline{N}$-bonded is clear. In all spectra, the strong, symmetric ONO^- stretching frequency occurs in the region 1020–45 cm^{-1}, no other absorption in the 1300 cm^{-1} region is evident except the expected single NH_3 δ_s peak, and the ρ_w band for $-NO_2^-$ near 600 cm^{-1} is absent.[145] The assignments of the observed bands are straightforward, with the exception of those in the 340–395 cm^{-1} region. However, Cleare and Griffith[146] are of the opinion that this band in $Cr(NH_3)_5ONO^{2+}$ is due to the metal-nitrito oxygen stretching frequency, so this assignment is assumed for all the nitrito-complexes listed.

(g)   Attempted Preparations of the cis-Chloronitritotetra-

aminechromium(III) Ion

All the trial experiments itemised below were unsuccessful :

(i)   A method similar to that for the preparation of the trans-isomer produced $\underline{cis}$-$[Cr(NH_3)_4(ONO)_2]ClO_4$ in excellent yield. The sample exhibited identical properties, spectrum, and analytical data to that prepared from $\underline{cis}$-$Cr(NH_3)_4(H_2O)_2^{3+}$. Repeat experiments carried out at $\underline{ca}$. 263 K in an ice/salt bath gave the same result.

(ii) Similar attempts to (i) at $\underline{ca}$. 250 K in methanol and mixed methanol/water solvent produced only starting material on addition of $NaClO_4$ solution.

(iii) Cl^-, SiF_6^- and $(C_6H_5)_4B^-$ failed to precipitate the required complex ion in an experiment similar to (i), but with ClO_4^- absent.

(iv) A solid-state method was tried involving heating $\underline{cis}$-$[Cr(NH_3)_4(H_2O)(ONO)]Cl_2$ in an oven at either 363 K or 393 K. After a few hours at either temperature, green, partially insoluble substances resulted. Analyses showed chromium contents of $\underline{ca}$.

30%, while very little nitrite remained. The spectra of the soluble fractions in acidic media showed broad, flat peaks centred at ca. 550 nm. These results appear to indicate decomposition with loss of nitrite and ammonia and possible formation of chromic oxide and polymeric species. The apparent decomposition is surprising, since this heating technique has been used with much success in the preparations of halo-amminechromium(III) complexes from aquo-ammine precursors[141,143,147-8].

(v) The reaction of cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ with an excess of nitrite ion was followed spectrophotometrically at several pH values in the range 3 to 5. No evidence for intermediates was detected and the spectrum of the product, on acidification, always corresponded with that of cis-$Cr(NH_3)_4(H_2O)_2^{3+}$.

(h)   Reactions of cis- and trans-Chloro-aquotetra-amminechromium(III)
Ions in Nitrite Buffer at pH 4

A nitrite buffer with the composition 0.5M $[NO_2^-]$ + 0.05M $[HNO_2]$, and a temperature of 293.1 K, were used in all runs. The reactions of the perchlorate salts of the complexes were followed both spectro-photometrically, scanning spectra at measured time intervals, and by Cl^- release using the chloride ion selective electrode. The trans-complex showed a reaction which was complete in ca. five minutes and displayed an isosbestic point at ca. 580 nm. The final spectrum had a peak at 533 nm (E_M ca. 30), but on acidification and the destruction of nitrous acid using hydrogen peroxide, the spectrum reverted to that of the starting complex, trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$. In acid solution, the oxidation of HNO_2 to NO_3^- by H_2O_2 is known to be rapid[149], but $Cr(III)$ is not oxidised. The observed reaction would appear to have been the formation of trans-$Cr(NH_3)_4(ONO)Cl^+$, since this species has an absorption peak at 535 nm (E_M 31.6) and the calculated isosbestic point for the spectral change is 582 nm. The reaction followed by Cl^- release showed that <5% of the co-ordinated chloride ion was lost in five minutes

and less than 50% over a period of one hour.

The same sequence of experiments with the cis-isomer gave completely different results. A reaction with a sharp isosbestic point at 517 nm was complete in 13 minutes, yielding products with a spectral peak at 491 nm (E_M ca. 57). Cis-$Cr(NH_3)_4(H_2O)ONO^{2+}$ has a peak at 491 nm (E_M 54), while λ_{max} = 492 nm (E_M ca. 65) for cis-$Cr(NH_3)_4(ONO)_2^+$. On acidification and treatment with H_2O_2, the spectrum of the product obtained agreed accurately with that of cis-$Cr(NH_3)_4(H_2O)_2^{3+}$. Following the reaction by the detection of chloride ion showed 100% loss of Cl^- from the complex within 13 minutes. The first-order rate constant for the reaction determined by Cl^- release (k_{obs} = 7.7 X $10^{-3}s^{-1}$) agreed well with that obtained from spectrophotometric measurements (k_{obs} = 7 X $10^{-3}s^{-1}$). Repeat experiments at pH 4 in the absence of nitrite ion showed that the release of Cl^- from cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ was very slow, and at least a factor of three less than the rate of dissociation from the trans-isomer under the same conditions.

The results of Section (h) demonstrate that nitrous acid catalysis of the aquation of cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ is prevalent at pH 4 as well as in more acidic solution. The reason for the failure to isolate the required complex, cis-$Cr(NH_3)_4(ONO)Cl^+$, from solution as described in Section (g) would appear to be that the species does not form in sufficiently high concentration. Indeed, it might be inferred from the solid state attempts at preparation that the required compound is inherently unstable.

4.8.   Conclusion

Evidence for the participation of nitrito-complexes in the nitrous acid catalysed aquations of halo-aquochromium(III) complexes has been presented in the earlier sections of this chapter. The lability with respect to loss of halogen of the intermediate proposed, when the nitrito and the leaving group are in a cis-relationship, has also been demonstrated for the catalysed aquation of cis-Cr(NH$_3$)$_4$(H$_2$O)Cl^{2+}. It is interesting to speculate on the reason for this latter observation. Basolo and Pearson[1c] attribute a strong cis-labilizing effect to the donation of electrons from filled π-orbitals on the ligand cis to the leaving group to the vacated lobe of the hybrid d^{2}sp^3 orbital on the metal ion. The authors propose that the interaction helps to stabilise the transition-state, which is illustrated in Figure 21. Before it is possible to decide if a similar effect occurs in the particular case studied here, it is necessary to consider the probable structure of a cis-CrL$_4$(ONO)X$^+$ complex (where X is a halo-ligand).

The length of the chromium-nitrito oxygen band is known for the compound $\angle$Cr(NH$_3$)$_5$ONO$\angle$Cl$_2$[150], but the more detailed study promised by Hansson and Bartin has not yet appeared in the literature, hence bond lengths and angles for the nitrito-ligand are assumed to be the same as in nitrous acid. The structure of trans-nitrous acid, which has a planar form, is shown in Figure 22. The internal trans-configuration is assumed for a co-ordinated nitrito-ligand, since this structure is dominant in free nitrous acid[126], and is presumably greatly preferred in complexes by steric considerations[94]. The published value[151] for the terminal Cr(III)——Cl distance in Cr$_2$Cl$_9$$^{3-}$ is used. The structure deduced for a cis-chloronitritochromium(III) complex with probable values of bond lengths (in Angstrom units, $\underline{A}$) and angles is illustrated in Figure 23, where the nitrito- and chloro- ligands are in the positions of closest approach. The H-O-N bond angle of 105° in trans-nitrous
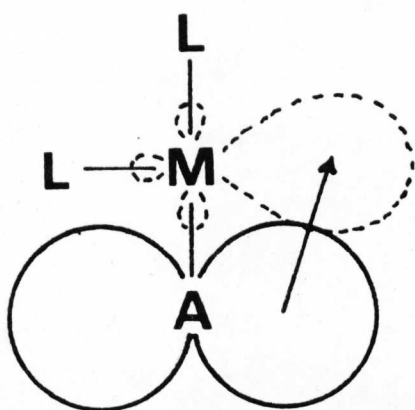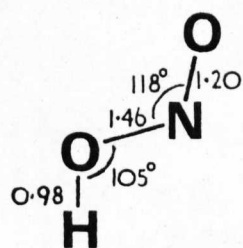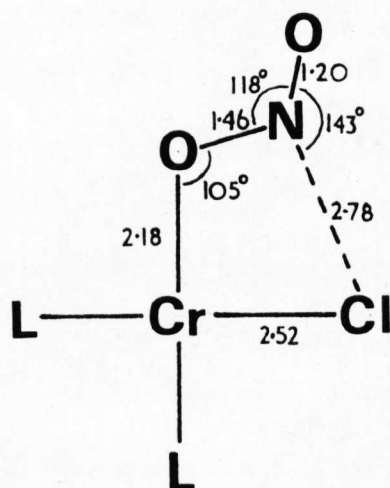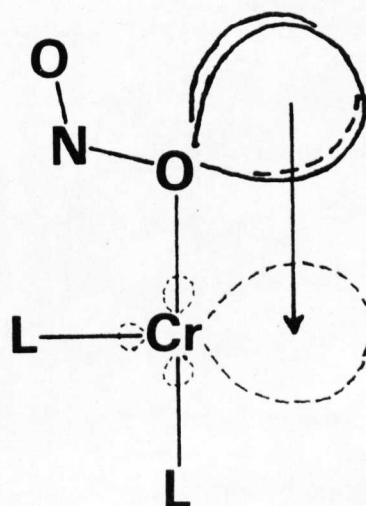
FIGURE 21
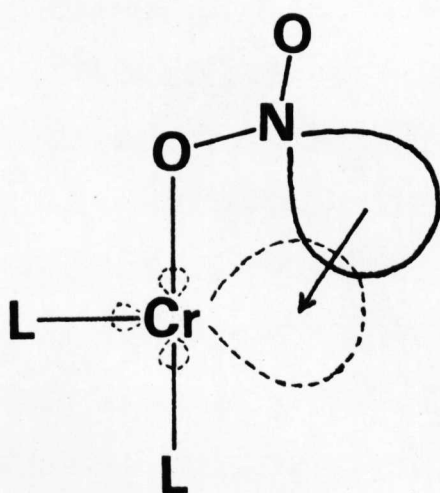

FIGURE 22

FIGURE 23

FIGURE 24

FIGURE 25
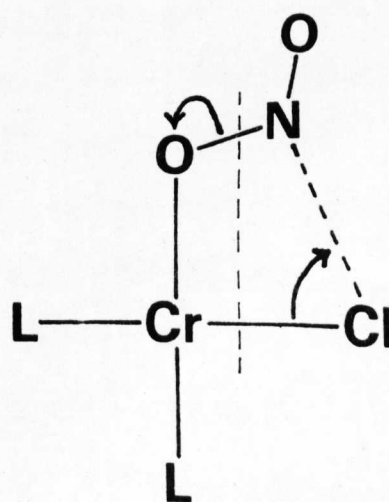

FIGURE 26

acid presumably indicates that the protonated oxygen atom has a sp^3 hybridised electron orbital configuration. If the same type of σ-bonding is involved in co-ordination to $Cr(III)$, then there is no filled π-orbital on the bonding oxygen atom which can feed electrons into the $Cr(III)$ d^2sp^3 orbital, as suggested by Basolo and Pearson. However, two other opportunities for overlap exist, which might lower the energy of the transition state as the halo-ligand dissociates. It may be possible for the lone pairs of electrons on the co-ordinated oxygen atom to interact with the vacant lobe on the $Cr(III)$ ion as shown in Figure 24, or the lone pair of the nitrito nitrogen atom may have a similar capability (Figure 25).

A cyclic transition state can also be envisaged, leading to the elimination of ClNO, and is illustrated in Figure 26. The N-Cl bond distance in ClNO has been determined[151] as 1.95 $\underline{A}$ and the bond angle as 116°. In $\underline{cis}$-$CrL_4(ONO)Cl^+$, on purely geometric considerations, the nitrito nitrogen atom and the chloro-ligand can approach to well within 1 $\underline{A}$ of the bonding distance, as can be seen in Figure 23. Repulsion between the chloro-ligand and the lone pair of the nitrogen atom might be expected to prevent the required orientation of the nitrito-ligand, but polarisation of the -O-N bond, as shown in Figure 26, could lessen this effect. To complete the elimination mechanism, the co-ordinated oxygen atom remaining would require protonation, while a water molecule from the outer-sphere of the complex could replace the chloro-ligand. Evidence for or against this intramolecular elimination reaction might be obtained by the study of other acido-penta-aquochromium(III) complexes. Bisulphate ion and NO^+ are known[152] not to form a covalent species, in contrast to nitrosonium and halide ions. Hence, it would be interesting to see if catalysis by nitrous acid occurs for the aquation of $Cr(H_2O)_5SO_4^+$ [40] in acidic solution. If catalysis were observed, it would indicate that intramolecular elimination is probably not involved.

However , lack of catalysis would not necessarily be confirmation of the mechanism, since the sulphato-ligand is much more bulky than a halo-group and unfavourable steric effects might come into play.   It could also be informative to study the aquation of $Cr(H_2O)_5NCS^{2+}$ in the presence of nitrous acid.   HONCS is thought to be covalent[152], so catalysis should occur, but the oxidation of free NCS^- (and maybe even the co-ordinated ligand) would be a problem.

The possible mechanisms advanced to explain the ease of dissociation of chloride ion from a cis-chloronitritochromium(III) complex are not intended to necessarily exclude others, and probably no mechanism is capable of proof in the absence of an isolable complex.   However, because of the great disparity in the apparent stabilities of cis- and trans-$Cr(NH_3)_4(ONO)Cl^+$, the intramolecular elimination process seems the most attractive explanation.   If the orbital overlap suggestion, outlined above, were the sole explanation for the rapid dissociation of Cl^-, then any group cis to a nitrito-ligand should be labilised. Though there is evidence that aquo-amminechromium(III) complexes tend to lose ammonia in aqueous solution somewhat more rapidly in the presence of HNO_2 (as mentioned above), and though it has been observed that cis-$Cr(NH_3)_4(ONO)_2^+$ is more labile than the trans-isomer, the magnitudes of these differences appear to be much smaller than the apparent relative stabilities of the two $Cr(NH_3)_4(ONO)Cl^+$ complexes.

CHAPTER 5

THE ACID CATALYSED AQUATIONS
OF NITRITOCHROMIUM(III) COMPLEXES

5.1   Introduction

The mechanism postulated in Chapter 4 for the nitrous acid
catalysed aquations of halo-aquochromium(III) complexes requires a
rapid acid catalysed reversion of the nitrito-intermediate to the
starting complex.   It was therefore a surprise to find that Holba[153]
reports the rate of reaction 5(i) to be slow and independent of acid
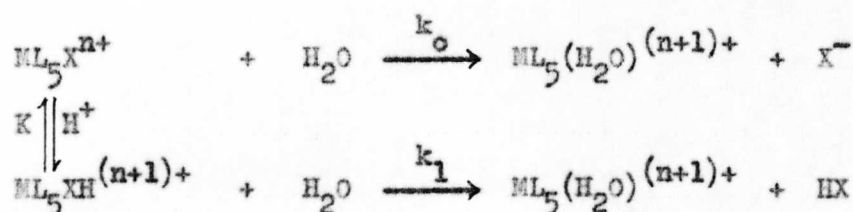concentration in the range 0.005 – 0.5M at temperatures 303 – 343 K.

$$Cr(NH_3)_5ONO^{2+} + H_3O^+ \longrightarrow Cr(NH_3)_5H_2O^{3+} + HNO_2 \underline{\quad\quad} 5(i)$$

Holba's work prompted the investigation of the acid hydrolyses of
nitritochromium(III) complexes which is described in this chapter.
In contrast to Holba's findings, the aquation rates of $Cr(NH_3)_5ONO^{2+}$
and four other nitritochromium(III) complexes in acid solution were
found to be rapid and dependent on acid concentration.   A possible
reason for the discrepancy will be discussed later.   As described in
Chapter 1, a ligand in an octahedral complex is liable to acid catalysed
hydrolysis if it is highly basic or can hydrogen bond[1c].   In addition
to the examples mentioned in Chapter 1 involving $-NO_2^-$, F^-, N_3^-, SO_4^{2-},
and $-CN^-$ ligands in Cr(III) and Co(III) complexes[35-41], acid catalysis
has been noted for the aquations of carbonato-[154] and phosphato-complexes[155]
of Co(III), and acetato-[156] and hypophosphito-complexes[157] of Cr(III).
The mechanism of the catalysis is thought to involve protonation of the
co-ordinated ligand which inductively weakens either the metal-ligand
bond, or, in a few cases, an internal bond of the ligand.   The following
mechanism is typical for the aquation of a complex subject to acid
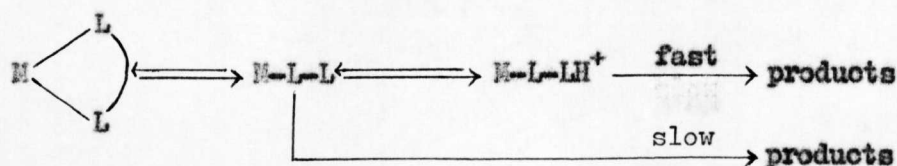catalysis :

$$ML_5X^{n+} \quad + \quad H_2O \xrightarrow{k_o} ML_5(H_2O)^{(n+1)+} \quad + \quad X^-$$

$$K \updownarrow H^+$$

$$ML_5XH^{(n+1)+} \quad + \quad H_2O \xrightarrow{k_1} ML_5(H_2O)^{(n+1)+} \quad + \quad HX$$

This mechanism exhibits the following rate law :

$$d[ML_5X^{n+}]/dt = (k_o + k_1 K/[H^+])[ML_5X^{n+}]$$

Other terms inverse order in acid concentration can sometimes be present in the rate law[37,40-1]. That metal-ligand bond cleavage does not occur for the acid catalysed pathway of the aquation of $Co(NH_3)_5 OCO_2^+$ has been demonstrated[158] by experiments in ^{18}O-labelled water, since very little ^{18}O is incorporated in the products, $Co(NH_3)_5 H_2 O^{3+}$ and CO_2. This type of process is also thought to occur in the acid hydrolyses of $Cr(H_2O)_5 OCOCH_3^{2+}$ [156], the nitritochromium(III) complexes described in this work, and possibly $Cr(H_2O)_5 H_2 PO_2^{2+}$ [157].

The hydrolyses of complexes containing chelating ligands are often acid catalysed[1c]. Examples demonstrating this behaviour include $Fe(bipy)_3^{2+}$, $Ni(en)_3^{2+}$ and $Ni(bipy)_3^{2+}$ [159]. The catalysis is thought to arise from the protonation of a partially-co-ordinated chelate ligand:

Nitrite ion is a potential bidentate ligand, since the two oxygen atoms are equivalent. It is conceivable that two nitrito-complexes involved in this study, which are thought to have the formulae $Cr(H_2O)_5 ONO^{2+}$ and cis-$Cr(NH_3)_4(H_2O)ONO^{2+}$, could, perhaps, contain a bidentate nitrite ligand However, this possibility is remote since it has been suggested[40] that, for a rigid octahedral structure to contain a bidentate oxyanion, the O-O distance must be at least 2.56 $\underline{A}$. The oxygen atoms of NO_2^- are separated by only 2.09 $\underline{A}$ [151]. Also, the nitritochromium(III) complexes mentioned above display very similar properties to those of the other complex ions studied, $Cr(NH_3)_5 ONO^{2+}$, trans-$Cr(NH_3)_4 Cl(ONO)^+$, and

<u>cis</u>-$(NH_3)_5Cr-OH-Cr(NH_3)_4ONO^{4+}$, which must all contain a monodentate nitrito-group.

The isolation in solution of the complex ion, $Cr(H_2O)_5ONO^{2+}$, is reported for the first time in this study. This species was postulated to be an intermediate in the inner-sphere reduction of the nitropenta-amminecobalt(III) ion by $Cr(II)$[160] :

$$Co^{III}NO_2 + Cr^{II} \longrightarrow Co^{II} + ONOCr^{III}$$
$$Cr^{III}ONO + Cr^{II} \longrightarrow Cr^{III} + {}^{\bullet}O_2NCr^{III}$$
$$Cr^{III}NO_2{}^{\bullet} + Cr^{II} \xrightarrow{2H^+} Cr^{III}NO + H_2OCr^{III}$$

(ammine- and aquo-ligands have been omitted for clarity)

Garnier[161] has demonstrated that stepwise formation of three nitrito-complexes, $Cr(H_2O)_{(6-n)}(ONO)_n^{(3-n)+}$ (where n = 1 to 3), occurs when hexa-aquochromium(III) ion reacts in strong nitrite buffers. A value of 63 was reported for the formation constant of $Cr(H_2O)_5ONO^{2+}$ at I = 2.5 and a temperature of 298.1 K. Though the **trinitritotri-aquochromium**(III) complex was isolated as a solid, the mononitrito-ion was not separated from the equilibrium mixture. $Cr(H_2O)_5ONO^{2+}$ could also be an intermediate in the nitrous acid catalysed aquations of chloro- and bromopenta-aquochromium(III) ions described in Chapter 4. Though the intimate mechanism for the elimination of the halo-ligand from the suggested halonitritotetra-aquochromium(III) intermediate was not elucidated, it is possible that the nitrito-group remains co-ordinated until after the halo-ligand has dissociated, and is then rapidly aquated because of the acidic conditions employed.

5.2. <u>Experimental</u>

(a) <u>Preparation of Nitritopenta-amminechromium(III) Perchlorate</u>

The nitrate salt of the complex ion was prepared by a published method[134]. While attempting to convert the nitrate to the perchlorate salt by a reported technique, it was observed that there was a strong tendency for the complex to decompose with loss of ammonia molecules.

The pH of a saturated aqueous solution rose quite rapidly at room temperature, even in the dark, and after a few hours an undetermined blue solid precipitated. An aqueous solution of the complex (ca. 10^{-2}M) was also observed to suffer decomposition while recording the visible spectrum at 293 K. Buffering at pH 3-4 with solutions of phthalate, acetate, or 4-bromopyridine, and at pH 8.5 with a 0.5M ammonia-ammonium perchlorate buffer failed to stabilise the complex. The initial decomposition in 1M 4-bromopyridine (pH 4) occurred with an isosbestic point at ca. 497 nm. Reaction 5(i) was later observed to proceed without an isosbestic point in the range 400 - 530 nm. After approximately 90 minutes at pH 4 and room temperature, the decomposition reaction no longer showed an isosbestic point. These observations are consistent with a stepwise loss of co-ordinated ammonia molecules from the complex. Similar observations have been reported for other complex ions of the type $Cr(NH_3)_5X^{2+}$ ($X^- = F^-$, Cl^-)[162-3], and with $Cr(NH_3)_6^{3+}$ and $Cr(NH_3)_5H_2O^{3+}$ [142] in acidic solutions.

To avoid this decomposition, the perchlorate salt of the complex ion was prepared by a different procedure at low temperature. The nitrate salt (1.5g), dissolved in ice-cold 0.01M acetic acid (500 ml), was filtered to remove traces of undissolved material, and precipitated by a filtered solution of sodium perchlorate in a minimum volume of ice-cold water. Yield 1g. (Analysis. Found : Cr, 13.6% ; N, 21.6% ; NO_2^-, 11.6%. Calc. for $[Cr(NH_3)_5ONO](ClO_4)_2$: Cr, 13.6% ; N, 22.0% ; NO_2^-, 12.0%). The visible spectrum of the complex was obtained in water at 275 K immediately after dissolution of the solid perchlorate salt. Parameters found were : λ_{max} 355 nm (E_M 79.4) and λ_{max} 477 nm (E_M 47.2). The U.V. peak agrees excellently with that reported[164], but Linhard et al. quote a visible maximum of 482 nm (E_M 42.7). The spectral particulars reported here were checked several times with different samples of the complex and the parameters were always found to be the same within experimental error, as those quoted. Possibly

the sample of Linhard et al[164] suffered some decomposition before the visible peak could be recorded, since, as no mention was made to the contrary, the solution of the complex was probably at room temperature.

(b)   Preparation of the Nitritopenta-aquochromium(III) Ion

The ion $Cr(H_2O)_5ONO^{2+}$ was isolated by a cation-exchange procedure from an equilibrium mixture of nitrito-aquo-complexes formed by buffering $Cr(H_2O)_6^{3+}$ in a ten-fold excess of nitrite ion at pH 3-4. 1M $HClO_4$ (50 ml) was added to hexa-aquochromium(III) perchlorate (5.7g, prepared by a published method[125], and dried by pressing between filter papers).   The solution was cooled to 273 K and added rapidly, with stirring, to an ice-cold solution of sodium nitrite (8g) in water (450 ml). The stoppered solution was allowed to equilibrate for 15 minutes over ice.   A jacketed column (2.5 X 28 cm) of Dowex 50WX2 (100 - 200 mesh) cation-exchange resin in the Na^+ form was pre-washed with 0.1M $NaClO_4$ solution (250 ml), which contained 2×10^{-4}M $HClO_4$.   On top of the column was fitted a long reflux condenser, and both the column and the condenser were maintained at ca. 273 K by a flow of water from an ice-water bath.   The complex solution was transferred to the column and the positive species concentrated at the top of the resin using a drop rate of ca. one per second.   When all the solution had passed onto the column, excess nitrous acid and nitrite ion, and complexes of charge zero and +1, were quickly eluted with pre-cooled 0.2M $NaClO_4$ solution (100 ml) which contained 2×10^{-4}M $HClO_4$.   The violet mononitrito-complex was separated from the blue hexa-aquochromium(III) ion by eluting quickly with a pre-cooled 0.8M $NaClO_4$ solution at pH 3.7 ($HClO_4$).   It is necessary to separate the violet band as quickly as possible, since the nitrito-complex reverts to $Cr(H_2O)_6^{3+}$ in the absence of an excess of HNO_2.

Attempts to isolate a solid derivative by the use[125,144] of large counter-ions of charge -2 failed, possibly because it was difficult to obtain a solution more concentrated than ca. 10^{-2}M from the ion-exchange

preparation. It is impossible to concentrate the complex since it is unstable with respect to temperature and pH changes. The half-life for decomposition at 276 K and pH 3.2 is ca. 100 minutes. Solutions of the complex were frozen immediately after elution, and stored for future use in stoppered tubes at ca. 200 K. Analysis of the $Cr : NO_2^-$ ratio of the species in solution was taken as an indication of the purity of samples prepared. In all cases the ratio was $1 : (1.00 \pm 0.05)$ which, combined with the observed ion-exchange behaviour consistent with that of a +2 charged species, showed that the chromium complex in solution was $Cr(H_2O)_5ONO^{2+}$. Two typical sets of analysis figures are given below :

$[Cr]/mM$	$[NO_2^-]/mM$	$[Cr] : [NO_2^-]$
6.57 ± 0.03	6.3 ± 0.2	$1 : 0.96 \pm 0.03$
7.05 ± 0.03	7.17 ± 0.06	$1 : 1.02 \pm 0.01$

The U.V. and visible spectrum of the complex ion was recorded at 280 K immediately after eluting a sample from the ion-exchange column. The same spectrum was obtained at several pH values in the range 3.0 – 3.7, which indicates that significant concentrations of hydroxy species were absent. A typical spectrum of the nitrito-complex in a solution at pH 3.7 is illustrated in Figure H of Appendix 1, together with the spectra of $Cr(H_2O_6)^{3+}$ and NO_2^-, for comparison. Absorption maxima for $Cr(H_2O)_5ONO^{2+}$ were observed at 365 nm (E_M 44.8) and 563 nm (E_M 18.1), minima at 337 nm (E_M 35.0) and 474 nm (E_M 4.7), and shoulders at ca. 372 nm (E_M ca. 44), ca. 410 nm (E_M ca. 21) and ca. 670 nm (E_M ca. 2). The peak at 365 nm shows slight evidence of fine structure. Vibrational fine structure of nitrito-ligands has been noted for other complexes, particularly in non-aqueous solvents[94]. The visible spectrum of $Cr(H_2O)_5ONO^{2+}$ was deduced by Garnier from the equilibrium studies mentioned in Section 5.1. The calculated peak position and intensity (565 nm, E_M 19) agrees very well with the value obtained experimentally

in this study (563 nm, E_M 18.1).

(c)   Preparations of trans-Chloronitritotetra-amminechromium(III)

Perchlorate and cis-Nitrito-aquotetra-amminechromium(III) Chloride

These complexes were prepared by the methods already described in Sections 4.7(f) and 4.7(e) respectively.

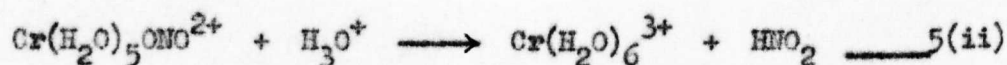(d)   Preparation of cis-Nitritoerythrochromium(III) Perchlorate

The complex cis-$[(NH_3)_5Cr-OH-Cr(NH_3)_4ONO]Cl_2 \cdot (ClO_4)_2 \cdot H_2O$ was prepared by a published method[165]. The mixed perchlorate-chloride salt was converted to the perchlorate by dissolving the complex in the minimum possible volume of water, adding two equivalents of $AgClO_4$, centrifuging off the resulting precipitate of $AgCl$, and throwing down the required salt by the addition of saturated $NaClO_4$ solution. (Analysis. Loss of weight on drying at 380 K, 2.3%. Calc. for one molecule of water of crystallisation, 2.4%. Found : Cr, 14.1% ; NO_2^-, 5.9%. Calc. for $[(NH_3)_5Cr-OH-Cr(NH_3)_4ONO](ClO_4)_4 \cdot H_2O$: Cr, 14.1% ; NO_2^-, 6.2%). The complex ion is assigned the cis-configuration since the parent aquo-erythrochromium(III) ion has been shown to have this form[141]. Figure J of Appendix 1 illustrates the visible spectrum of the binuclear complex recorded immediately after dissolution in water at ca. 283 K. Spectral parameters were determined to be : λ_{min} 304 nm (E_M 67.0), shoulder ca. 325 nm (E_M ca. 73), λ_{max} 368 nm (E_M 114), shoulder ca. 376 nm (E_M ca. 112), λ_{min} 428 nm (E_M 28.2), λ_{max} 502 nm (E_M 106).

(e)   Kinetic Determinations

Stoicheiometric experiments demonstrated that, in the presence of at least a ten-fold excess of acid, the aquations of the nitrito-complexes were rapid and proceeded to completion producing the corresponding aquo-complex + one equivalent of HNO_2. Rapid flow experiments at 273.7 K using 1M $HClO_4$ failed to indicate any protonation of the nitrito-complexes prior to aquation. The acid hydrolyses of the complexes were studied in the range of temperature 273 – 303 K. Higher

temperatures were not possible because of the instability with respect to loss of ammonia of the amine complexes, and the background aquation of $Cr(H_2O)_5ONO^{2+}$. Fresh solutions of the complexes were prepared using ice-cold water for each set of kinetic runs. These solutions were stored on ice in darkened flasks and were discarded before significant decomposition could occur. Thermostatting times were kept to a minimum consistent with accurate temperature control.

Perchloric acid in the concentration range 0.01 - 1.00M was used, and kinetic runs were carried out under pseudo first-order conditions. Kinetic determinations at the higher acid concentrations were made using the stopped-flow technique, but the slower reactions at lower acidities required the use of the more conventional method using syringe injection described in Section 2.3(2). A fixed wavelength of 240 nm was employed for all determinations. The nitrito-complexes absorb strongly at this wavelength and very low concentrations of the order of 10^{-4}M could be employed. At such low concentrations the products of the aquation, aquo-complex and nitrous acid, have little absorption at 240 nm, so large changes of absorbance (ca. 0.2 - 0.6) were easily obtainable on reaction. The absorbances of reactant and products in the wavelength range 200 - 250 nm are illustrated in the inset of Figure M (Appendix 1) for the reaction :

$$Cr(H_2O)_5ONO^{2+} + H_3O^+ \longrightarrow Cr(H_2O)_6^{3+} + HNO_2 \underline{\qquad} 5(ii)$$

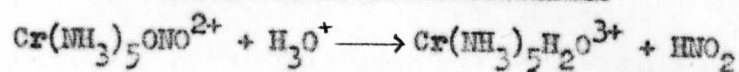The aquations of the other nitrito-complexes exhibit similar absorbance changes.

5.3. Results

Good first-order rate plots were observed in all experiments to >90% completion of reaction. The observed rate constants (means of at least three determinations) obtained for the aquations of the nitrito-complexes at various acid concentrations and temperatures are listed in Tables 9 ($Cr(NH_3)_5ONO^{2+}$), 10 ($Cr(H_2O)_5ONO^{2+}$),

TABLE 9

Kinetic data for the reaction :

$$Cr(NH_3)_5ONO^{2+} + H_3O^+ \longrightarrow Cr(NH_3)_5H_2O^{3+} + HNO_2$$

[Complex] $\underline{ca.}$ 3×10^{-4}M, I $\approx$ 1.0 (NaClO$_4$)

Temperature (K)	$[H^+]$(M)	$10^3 k_{obs}(s^{-1})$	$10^2 k_{obs}/[H^+](M^{-1}s^{-1})$
276.1	0.045	0.92	2.02
"	0.099	1.97	1.99
283.1	0.011	0.49	4.45
"	0.028	1.47	5.25
"	0.047	2.56	5.45
"	0.071	3.74	5.27
"	0.099	5.11	5.17
"	0.200	11.0	5.50
"	0.300	19.8	6.60
"	0.400	25.1	6.28
"	0.500	34.6	6.92
"	"	37.0[a]	--
"	"	35.0[b]	--
"	0.600	41.1	6.85
"	0.650	55.3	8.51
"	0.700	51.3	7.33
"	0.800	84.9	10.6
"	0.900	98.9	11.0
"	0.990	102	10.3
290.1	0.048	6.21	13.0
"	0.100	13.9	13.9

(a) Ionic strength adjusted with LiClO$_4$

(b) In presence of 1.6×10^{-3}M [HNO$_2$] (10 X [Complex]).

Runs (a) and (b) excluded from calculations of k_1' and k_2'

TABLE 10

Kinetic data for the reaction :

$$Cr(H_2O)_5ONO^{2+} + H_3O^+ \longrightarrow Cr(H_2O)_6^{3+} + HNO_2$$

[Complex] ca. 5×10^{-4} M, $I = 1.0$ (NaClO$_4$)

Temperature (K)	$[H^+]$ (M)	$10^2 k_{obs}$ (s^{-1})	$k_{obs}/[H^+]$ (M^{-1}s^{-1})
273.7	0.100	1.39	0.139
"	0.300	6.63	0.221
"	0.600	21.1	0.351
"	0.993	62.7	0.631
283.1	0.0114	0.345	0.303
"	0.0216	0.706	0.327
"	0.0300	1.16	0.386
"	0.0400	1.59	0.397
"	0.0500	2.07	0.413
"	0.0600	2.53	0.421
"	0.0800	3.50	0.437
"	0.100	4.66	0.466
"	0.150	7.86	0.524
"	0.200	11.1	0.553
"	0.300	20.5	0.684
"	0.400	31.2	0.779
"	0.500	45.0	0.900
"	0.600	59.4	0.990
"	0.700	81.2	1.16
"	0.800	104	1.30
"	0.900	129	1.43
"	0.993	158	1.60
290.5	0.050	4.64	0.927
"	0.300	43.3	1.44
"	0.600	120	2.00

Temperature (K)	$[H^+]$ (M)	$10^2 k_{obs}$ (s^{-1})	$k_{obs}/[H^+]$ $(M^{-1}s^{-1})$
290.5	0.993	318	3.20
298.1	0.050	11.7	2.34
"	0.300	97.5	3.25
"	0.600	277	4.61
"	0.993	652	6.56

TABLE 11

Kinetic data for the reaction :

$$\text{trans-Cr(NH}_3)_4\text{Cl(ONO)}^+ + \text{H}_3\text{O}^+ \longrightarrow \text{trans-Cr(NH}_3)_4\text{Cl(H}_2\text{O)}^{2+} + \text{HNO}_2$$

[Complex] ca. 3×10^{-4}M, I = 1.0 (NaClO$_4$)

Temperature (K)	$[\text{H}^+]$ (M)	$10^3 k_{obs} (s^{-1})$	$10^3 k_{obs}/[\text{H}^+] (\text{M}^{-1}\text{s}^{-1})$
273.7	0.102	1.06	10.4
"	0.188	2.37	12.6
"	0.370	6.45	17.4
"	0.600	13.6	22.7
"	0.800	23.2	29.0
283.1	0.0511	1.56	30.5
"	0.102	3.46	33.9
"	0.201	7.49	37.2
"	0.301	12.7	42.2
"	0.400	20.3	50.8
"	0.500	30.0	60.0
"	0.600	38.3	63.8
"	0.800	60.6	75.8
"	0.975	84.7	86.9
293.1	0.0100	0.939	93.9
"	0.0209	2.05	98.2
"	0.0512	5.20	102
"	0.102	10.7	105
"	0.200	24.0	120
"	0.300	40.3	134
"	0.400	61.9	155
"	0.500	84.8	170
"	0.600	113	189
"	0.800	175	219

Temperature (K)	$[H^+]$ (M)	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}/[H^+]$ (M^{-1}s^{-1})
293.1	0.975	246	252
303.1	0.050	16.6	332
"	0.100	33.3	333
"	0.200	78.3	391
"	0.300	128	425
"	0.400	185	462
"	0.500	241	482
"	0.600	327	545
"	0.800	480	600
"	1.00	708	708

TABLE 12

Kinetic data for the acid-catalysed hydrolyses

of two nitritochromium(III) complexes

[Complex] ca. 5×10^{-4} M, I = 1.0 (NaClO$_4$), Temperature = 283.1 K

Complex	[H$^+$](M)	$10^2 k_{obs}$(s^{-1})	$10^2 k_{obs}$/[H$^+$](M^{-1}s^{-1})
cis-Cr(NH$_3$)$_4$(H$_2$O)ONO^{2+}	0.20	1.74	8.70
"	0.40	4.41	11.0
"	0.60	8.07	13.5
"	0.80	12.9	16.2
"	1.00	19.0	19.0
cis-(NH$_3$)$_5$Cr-OH-Cr(NH$_3$)$_4$ONO^{4+}	0.10	0.390	3.90
"	0.50	2.50	5.00
"	1.00	6.48	6.48

11 (trans-$Cr(NH_3)_4Cl(ONO)^+$) and 12 (cis-$Cr(NH_3)_4(H_2O)ONO^{2+}$ and cis-$(NH_3)_5Cr$-OH-$Cr(NH_3)_4ONO^{4+}$). To check that the reverse (i.e formation) reaction could be neglected under the conditions used in the kinetic experiments, some runs with $Cr(NH_3)_5ONO^{2+}$ were repeated in the presence of added sodium nitrite in ten-fold excess over the complex concentration. As can be seen from Table 9, the hydrolysis rate was not affected. Though the rate laws for the aquations of the complexes seem to be roughly first-order in acid concentration below 0.1M $[H^+]$, large deviations become evident above this acidity, the order with respect to $[H^+]$ becoming >1. This behaviour is most marked for $Cr(H_2O)_5ONO^{2+}$, and is illustrated using the data at 283.1 K in curve A of Figure 27. The observed rate constants for a particular complex at a certain temperature were fitted by means of a non-linear least-squares procedure using computer program ROO2/05 (Appendix 2) to the function :

$$k_{obs} = k_o + k_1^{'} [H^+] + k_2^{'} [H^+]^2$$

Good fits to the data were obtained, and, for every complex, values of k_o were found to be zero to within one standard deviation, showing that the contribution of the acid independent term to the observed reaction rate is negligible above 0.01M $[H^+]$.

The same rate law for the aquations of all the nitrito-complexes thus applies :

$$-d[Complex]/dt = (k_1^{'} [H^+] + k_2^{'} [H^+]^2)[Complex]$$

A linear relationship between k_{obs} and $[H^+]$ can be perceived :

$$k_{obs}/[H^+] = k_1^{'} + k_2^{'} [H^+] \underline{\qquad} 5(iii)$$

Plots of $k_{obs}/[H^+]$ versus $[H^+]$ are linear in all cases, showing that k_o is indeed negligible and that only powers in $[H^+]$ of 1 and 2 are involved in the rate law. The plots for data at 283.1 K are shown in Figure 27 for $Cr(H_2O)_5ONO^{2+}$ (line B) and $Cr(NH_3)_5ONO^{2+}$ (line C), and in Figure 28 for trans-$Cr(NH_3)_4Cl(ONO)^+$ (line A) and

FIGURE 27

Kinetics of the acid-catalysed hydrolyses of the

nitritopenta-aquochromium(III) ion (curves A and B)

and the nitritopenta-amminechromium(III) ion (curve C)

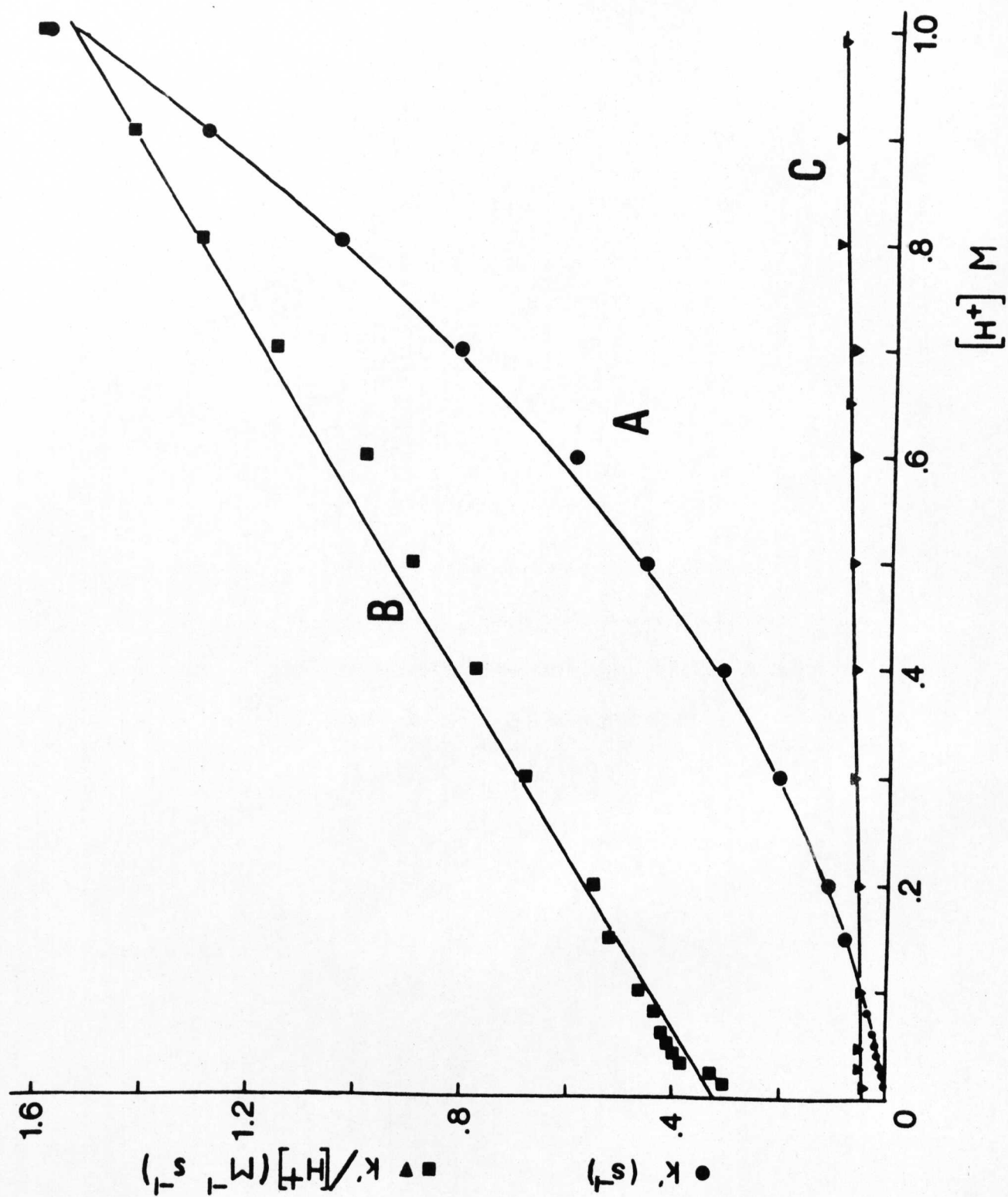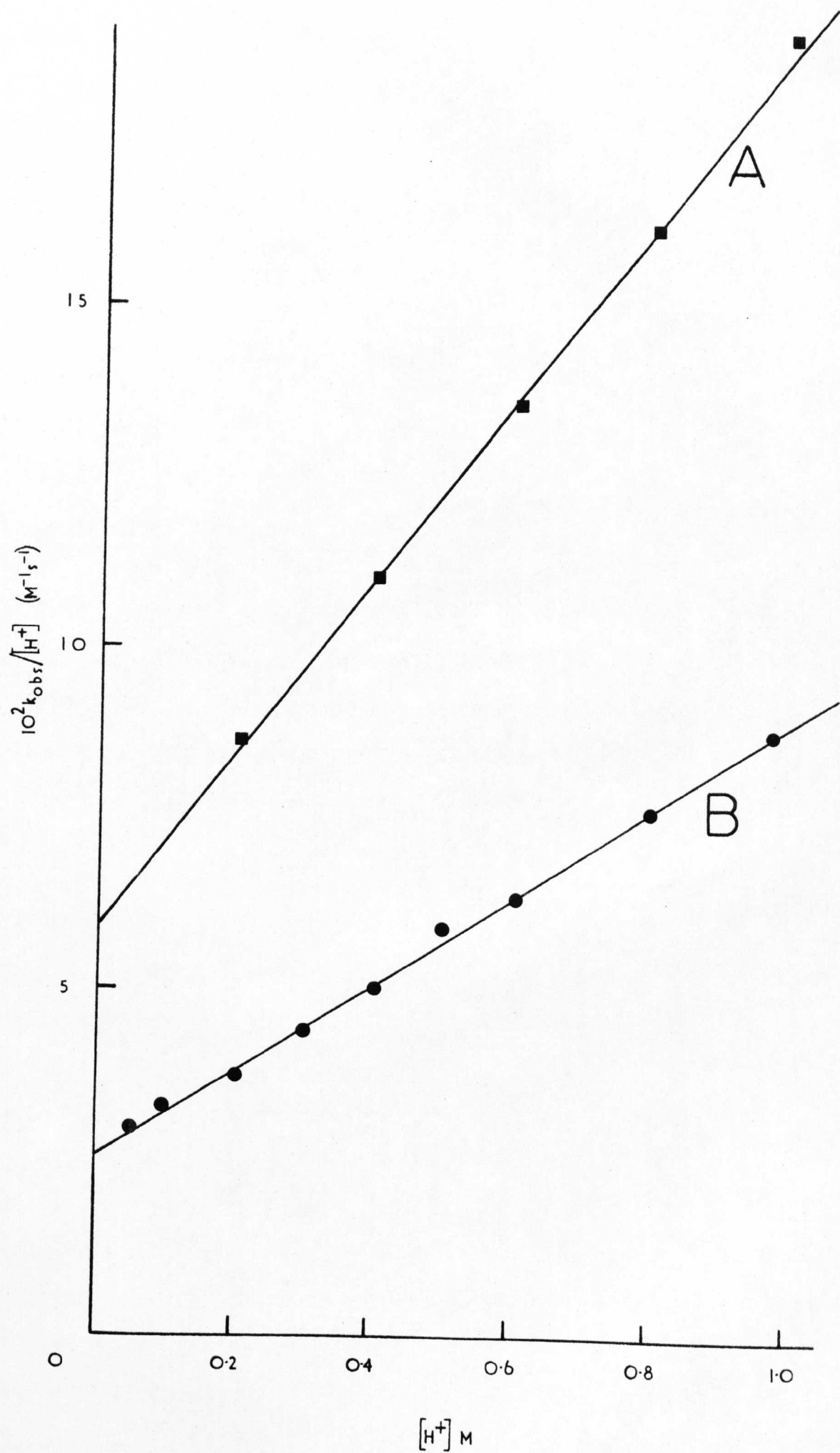at 283.1 K and I = 1.0 (NaClO$_4$)

FIGURE 28

Kinetics of the acid-catalysed hydrolyses of the
cis-nitrito-aquotetra-amminechromium(III) ion (curve A) and
the trans-chloronitritotetra-amminechromium(III) ion (curve B)
at 283.1 K and I = 1.0 (NaClO$_4$)

cis-$Cr(NH_3)_4(H_2O)ONO^{2+}$ (line B). Least-squares analysis of the plots of $k_{obs}/[H^+]$ versus $[H^+]$ produced the values for k_1' and k_2' (with their associated uncertainties) listed in Table 13. In the cases of the complex ions $Cr(NH_3)_5ONO^{2+}$, $Cr(H_2O)_5ONO^{2+}$, and trans-$Cr(NH_3)_4Cl(ONO)^+$, for which kinetic determinations were carried out at more than one temperature, activation parameters were calculated as described in Section 2.4 for both the second and third-order rate constants, k_1' and k_2'. The values derived are presented in Table 14.

5.4. Conclusions

The low frequency band in the visible spectrum of $Cr(H_2O)_5ONO^{2+}$ can be assigned[166] to the spin-allowed transition $^4T_{2g} \longleftarrow {}^4A_{2g}$, the energy of which gives a direct measure of the ligand-field splitting parameter, Δ. Since the band lies at a shorter wavelength (563 nm) than that of $Cr(H_2O)_6^{3+}$ (575 nm), nitrite ion should be placed above water in the spectrochemical series. The opposite conclusion was reached from studies of t_{2g}^6 systems[166], but the observation for $Cr(H_2O)_5ONO^{2+}$ is in accord with the spectra of other nitritochromium(III) complexes reported in this work and elsewhere[94].

There can be no doubt from the kinetic data obtained that the aquations of nitritochromium(III) complexes are rapid in acidic media and that the reaction rates are dependent on acid concentration. The acid independent pathway for aquation is negligible above $0.01N$ $[H^+]$ and, since the rapid acid catalysed pathways are thought to involve O–N rather than Cr–O bond breaking (see below), the slow, acid independent reaction route probably involves Cr–O fission. It is probable that this latter pathway only proceeds at a rate comparable to that of loss of co-ordinated ammonia molecules for the ammine complexes. The hypophosphitopenta-aquochromium(III) ion is similar to the nitrito-complexes in the sense that the k_0 term is also missing from the rate law of the acid hydrolysis of this complex ion (at $[H^+] > 0.08M$).

TABLE 13

Variation with temperature of k_1' and k_2' (from expression 5(iii))

for the aquation of nitritochromium(III) complexes.

Complex	Temperature (K)	$10^2 k_1' (M^{-1}s^{-1})$	$10^2 k_2' (M^{-2}s^{-1})$
$Cr(NH_3)_5ONO^{2+}$	276.1	2.05 ± 0.06	a
"	283.1	4.55 ± 0.26	5.90 ± 0.52
"	290.1	12.1 ± 0.2	a
$Cr(H_2O)_5ONO^{2+}$	273.7	6.6 ± 1.4	54 ± 2
"	283.1	32.2 ± 0.7	123 ± 1
"	290.5	75 ± 4	238 ± 8
"	298.1	198 ± 6	455 ± 9
trans-$Cr(NH_3)_4Cl(ONO)^+$	273.7	0.76 ± 0.03	2.59 ± 0.06
"	283.1	2.59 ± 0.07	6.27 ± 0.13
"	293.1	9.03 ± 0.14	16.2 ± 0.3
"	303.1	30.5 ± 0.4	38.9 ± 0.8
cis-$Cr(NH_3)_4(H_2O)ONO^{2+}$	283.1	5.9 ± 0.2	12.9 ± 0.3
cis-$(NH_3)_5Cr-OH-Cr(NH_3)_4ONO^{4+}$	"	3.6 ± 0.2	2.9 ± 0.1

(a) Insufficient data

TABLE 14

Activation parameters for the acid-catalysed aquations

of some Cr(III) and Co(III) complexes

Temperature 298.1 K, I = 1.0

Complex	$\Delta H^{\ddagger}(k_1')^a$	$\Delta S^{\ddagger}(k_1')^b$	$\Delta H^{\ddagger}(k_2')^a$	$\Delta S^{\ddagger}(k_2')^b$	Reference
$Cr(NH_3)_5ONO^{2+}$	19.7 ± 0.8	$+5 \pm 3$	f	f	This work
$Cr(H_2O)_5ONO^{2+}$	19.8 ± 0.6	$+9 \pm 2$	13.9 ± 0.3	-9 ± 1	"
trans-$Cr(NH_3)_4Cl(ONO)^+$	20.3 ± 0.3	$+6 \pm 1$	14.7 ± 0.2	-12 ± 1	"
$Cr(H_2O)_5F^{2+}$	24.5	-12	-	-	38
$Cr(H_2O)_5{}^*OH^{2+}$ c	27.6	-	-	-	112
$Cr(H_2O)_5SO_4^+$	26.5	-1	-	-	40
$Cr(H_2O)_5OCOCH_3^{2+}$ d	19.6	-	-	-	156
$Cr(H_2O)_5H_2PO_2^{2+}$	18.1	-24	-	-	157
$Co(NH_3)_5OCO_2^+$ e	17.0	-0.5	-	-	154

(a) Units of kcal. mol^{-1}.

(b) In entropy units.

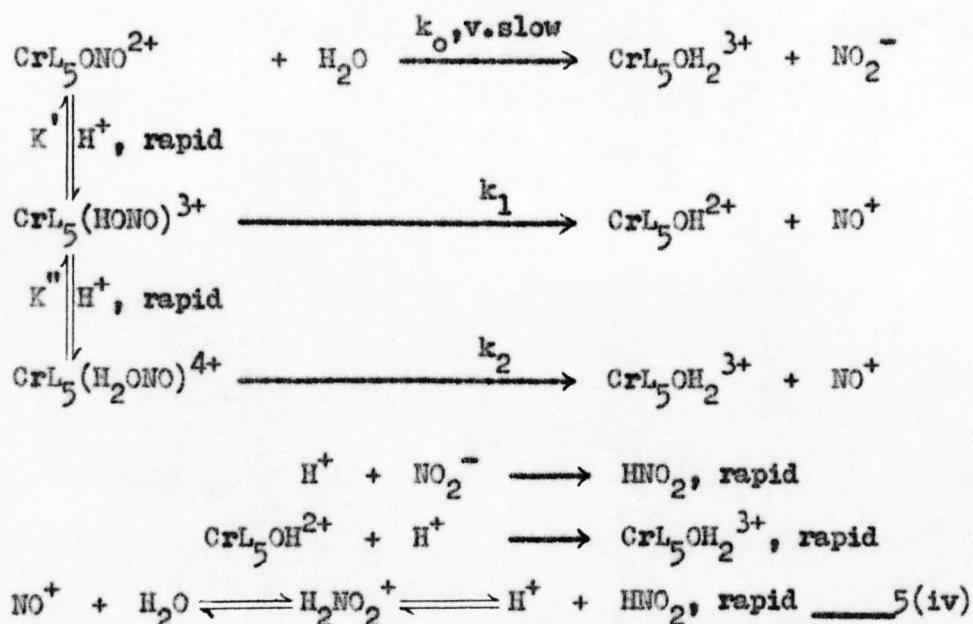(c) Water exchange rate of $Cr(H_2O)_6^{3+}$, I = 0.7.

(d) I = 4.0.

(e) I = 0.5.

(f) Insufficient data.

The results obtained in this study should be compared with those of Holba[153] for reaction 5(i). The rate constant reported by Holba at 323.1 K and 0.5M $[HClO_4]$ is more than two orders of magnitude smaller than the rate constant obtained in this work at 283.1 K and the same acidity. Holba's rates are similar to those reported for the loss of ammonia from $Cr(NH_3)_5H_2O^{3+}$ [142] and it is thus possible that this worker missed the rapid aquation of the nitrito-complex and merely followed the dissociation of NH_3 from the product of the reaction. The spectral changes reported by Holba in 0.01M $[HClO_4]$ are also dubious, showing no sign of the four large nitrous acid peaks[126] (at 346, 357, 371, and 385 nm) which were obtained in spectra of the aquation products in the present study.

The two terms in $[H^+]$ found in the rate law for the aquation of the nitrito-complexes indicate that pathways involving both single and double protonation of the complex are important. The following mechanism is consistent with the observed data :

$$CrL_5ONO^{2+} \quad + \quad H_2O \quad \xrightarrow{k_o, v.slow} \quad CrL_5OH_2^{3+} \quad + \quad NO_2^-$$

$$K' \Big\Vert H^+, \text{ rapid}$$

$$CrL_5(HONO)^{3+} \quad \xrightarrow{k_1} \quad CrL_5OH^{2+} \quad + \quad NO^+$$

$$K'' \Big\Vert H^+, \text{ rapid}$$

$$CrL_5(H_2ONO)^{4+} \quad \xrightarrow{k_2} \quad CrL_5OH_2^{3+} \quad + \quad NO^+$$

$$H^+ \quad + \quad NO_2^- \quad \longrightarrow \quad HNO_2, \text{ rapid}$$

$$CrL_5OH^{2+} \quad + \quad H^+ \quad \longrightarrow \quad CrL_5OH_2^{3+}, \text{ rapid}$$

$$NO^+ \quad + \quad H_2O \quad \rightleftharpoons \quad H_2NO_2^+ \rightleftharpoons H^+ \quad + \quad HNO_2, \text{ rapid} \underline{\quad\quad} 5(iv)$$

The values k_1' and k_2' deduced from the kinetic experiments are thus combined values of both rate and protonation equilibrium constants and have the relations :

$$k_1' = k_1 K' , \qquad k_2' = k_2 K' K''$$

where :

$$K' = [CrL_5(HONO)^{3+}]/[CrL_5ONO^{2+}][H^+]$$

$$K'' = [CrL_5(H_2ONO)^{4+}]/[CrL_5(HONO)^{3+}][H^+]$$

The activation parameters for k_1' and k_2' are also composite values, i.e. $\Delta H^{\ddagger}(k_1') = \Delta H^{\circ}(K') + \Delta H^{\ddagger}(k_1)$ and $\Delta H^{\ddagger}(k_2') = \Delta H^{\circ}(K') + \Delta H^{\circ}(K'') + \Delta H^{\ddagger}(k_2)$, where the constants in parentheses indicate the origin of the corresponding enthalpy term. Deutsch and Taube's[156] study of the more inert acetatopenta-aquochromium(III) ion gave a very small value for $\Delta H^{\circ}(K')$, ca. 1 kcal mol^{-1}. It seems reasonable to assume, therefore, that the values of $\Delta H^{\ddagger}(k_1')$ and $\Delta H^{\ddagger}(k_2')$ given in Table 14 are close to the values for k_1 and k_2 (within 1 or 2 kcal mol^{-1}).

The fact that spectrophotometric evidence for protonation of the nitrito-complexes before aquation was not obtained shows that the values of K' and K'' must be very small. Deutsch and Taube[156] quote K' for $Cr(H_2O)_5OCOCH_3^{2+}$ to be ca. 0.25. Since nitrite ion is ca. 40 times less basic than acetate ion, K' for $Cr(H_2O)_5ONO^{2+}$ should be much smaller than for the acetato-complex. Significant protonation would also lead to a more complex rate law being observed, with limiting behaviour tending to occur at high acidities. Such behaviour is exhibited, for example, in the acid catalysed aquation of $Co(NH_3)_5OCO_2^+$ [154]. A single acid catalysed step is observed and an expression :

$$k_{obs} = k_1K'[H^+]/(1 + K'[H^+])$$

In this particular case, K' is very large (ca. 3×10^6 at 298 K) and a limiting rate is reached at pH $\leq$ 4.

The existence of two mechanisms for the aquation of the nitrito-complexes, depending on singly and doubly protonated intermediates is unusual. Such a duality of mechanism has been described previously for di- and tetranitrocobalt(III) complexes[167-8]. However, in the cases of these nitro-complexes, the second proton was considered as being added to a different nitro-group to the first, a situation which is not applicable to the mononitrito-complexes studied in the present

work. For monophosphato-complexes of Co(III)[155], however, there is evidence that up to four protons can attach to a single phosphato-ligand. Deutsch and Taube[156] consider that the single protonation of the acetato-ligand in $Cr(H_2O)_5OCOCH_3^{2+}$ occurs at the co-ordinated rather than the terminal oxygen atom. If this is also true for nitrito-complexes, and if the Cr-O bond is not broken during the resulting reaction, the dissociation of NO^+ from the monoprotonated complex and retention of an OH^- ligand is easily envisaged, as written in reaction scheme 5(iv). A water molecule in the outer-sphere could perhaps assist dissociation by removing NO^+ in the form of $H_2NO_2^+$. The possible site for the attachment of the second proton in the diprotonated intermediate is not so easy to resolve, however. A double protonation of the co-ordinated oxygen atom of the nitrito-group would be the most attractive possibility, though this might not be energetically favourable. Protonation of the terminal oxygen of the nitrito-ligand in addition to that of the co-ordinated oxygen atom might possibly give rise to Cr-O bond cleavage and the elimination of $H_2NO_2^+$.

That the term in the rate law involving $[H^+]^2$ has a definite mechanistic significance is reasonable since the magnitude of k_2' is of the same order, or larger, than that of k_1'. A small increase in the second-order rate constant with increasing $[H^+]$ has been reported for the acid catalysed hydrolyses of $Cr(H_2O)_5CN^{2+}$ [41] and $Cr(H_2O)_5H_2PO_2^{2+}$ [157]. The results were interpreted by the application of an activity correction in the form of Harned's Rule[169]. It is doubtful if this correction can account for the observed variation of $k_{obs}/[H^+]$ with acid concentration for the aquations of nitritochromium(III) complexes, since, for example, a Harned coefficient, α_{H^+}, of ca. 0.9 would be required to explain the results for $Cr(H_2O)_5ONO^{2+}$ at 298.1 K, a much larger value than would appear reasonable. Activity coefficient data are, unfortunately, not available for the system $HClO_4 - NaClO_4$ under the conditions used in

this work. However, for the system HCl – NaClO$_4$ at 298.1 K and
I = 1.0, α_{H^+} was found[170] to be 0.024, and it is unlikely that α_{H^+} for
the couple HClO$_4$ – NaClO$_4$ could be much greater than this value. Since
it has been demonstrated[171] that deviations in the activity coefficient
of H$^+$ for the H$^+$ – Li$^+$ pair are less than those for the H$^+$ – Na$^+$ pair,
the experiments with Cr(NH$_3$)$_5$ONO^{2+} at 0.5M [H$^+$] and 283.1 K were
repeated using 0.5M [LiClO$_4$], instead of 0.5M [NaClO$_4$], to adjust the
ionic strength. The variation in k$_{obs}$ was not appreciable (see Table 9).

The rates of aquation observed for the nitrito-complexes are much
more rapid than almost all others known for Cr(III) complexes[1c], whether
acid catalysed or not. This, in itself, is good evidence that Cr–O
bond fission is not involved in the reactions, and further confirmation
can be gained by a comparison of $\Delta H^{\ddagger}(k_1')$ values for the aquations of
various Cr(III) and Co(III) complexes which are listed in Table 14.
The acid catalysed aquation of Cr(H$_2$O)$_5$F^{2+} must, of necessity, involve
chromium-ligand bond breaking, also the oxygen exchange rate of Cr(H$_2$O)$_6^{3+}$.
It would appear that the protonated sulphato-ligand of Cr(H$_2$O)$_5$SO$_4^+$
dissociates with Cr–O bond cleavage since the $\Delta H^{\ddagger}(k_1')$ value is similar
to those of the above reactions. The $\Delta H^{\ddagger}(k_1')$ values for the
nitritochromium(III) complexes, Cr(H$_2$O)$_5$OCOCH$_3^{2+}$ and Cr(H$_2$O)$_5$H$_2$PO$_2^{2+}$
are much lower, so it is reasonable that aquations proceed by a different
mechanism. The $\Delta H^{\ddagger}(k_1')$ value of 17 kcal mol^{-1} for Co(NH$_3$)$_5$OCO$_2^+$
supports this conclusion, since the acid catalysed aquation step is
known to proceed without Cr–O bond fission[158]. The dissociation of the
phosphato-ligand from Co(NH$_3$)$_5$H$_3$PO$_4^{3+}$ is thought to involve chromium-
oxygen bond cleavage[155], and the $\Delta H^{\ddagger}$ value is 26 kcal mol^{-1}. The
fact that the three nitritochromium(III) complexes all have very similar
$\Delta H^{\ddagger}(k_1')$ and $\Delta S^{\ddagger}(k_1')$ values is indicative that the non-reacting
ligands in the complex, and the charge on the complex, are not very
important in defining the energetics of aquation. This is further

confirmation that the reaction primarily involves the nitrito-ligand alone. The larger values of k_1' for the nitrito-complexes compared to those of $Cr(H_2O)_5OCOCH_3^{2+}$ and $Cr(H_2O)_5H_2PO_2^{2+}$ would appear to be a function of $\Delta S^{\ddagger}$, since the magnitudes of $\Delta H^{\ddagger}(k_1')$ are very similar. The low values of $\Delta H^{\ddagger}(k_2')$ for $Cr(H_2O)_5ONO^{2+}$ and trans-$Cr(NH_3)_4Cl(ONO)^+$ account for the importance of the term k_2' in the rate law of the aquations of these complexes. Cis-nitrito-erythrochromium(III) ion at 283.1 K produced similar kinetic data to that of $Cr(NH_3)_5ONO^{2+}$. This is expected since in acid solution the protonated oxygen bridge of the binuclear complex causes the two halves to behave almost as separate Cr(III) entities. This behaviour is in contrast to that observed in basic solution where internuclear molecular orbitals centred on the Cr-O-Cr bridge cause strong activation of the co-ordinated ligands, especially in the trans-position[1c].

Since the most likely leaving groups in the acid catalysed aquations of nitritochromium(III) complexes appear to be either NO^+ or $H_2NO_2^+$, by the principle of microscopic reversibility, the reverse reaction of nitrosation of a co-ordinated water molecule by NO^+ or $H_2NO_2^+$ must occur in acidic solution. This inference is in line with the work reported in Chapter 4, the aquations of halo-aquochromium(III) complexes catalysed by nitrous acid, for which the kinetic evidence indicates participation of such nitrosating agents as NO^+ and $H_2NO_2^+$ in forming the nitrito-intermediate in acidic solution, rather than N_2O_3 which is involved at ca. pH 4. The work reported in this chapter also justifies the two paths involving both one and two protons postulated in reaction scheme 4(i) for the reversion of the nitrito-intermediate to the starting complex. The rate constant k_{-1} in Chapter 4 corresponds to k_1' in this chapter, while k_{-2} and k_2' are similarly related.

Since nitrito-complexes of other metal ions (e.g. Co(III), Ir(III), Rh(III), and Pt(IV)[121]) are known , it would be interesting to investigate their acid hydrolyses, to see if the mechanism reported here for Cr(III) complexes is a general one.

APPENDIX 1

SPECTRA

FIGURE A

Spectral changes accompanying the aquation of the

bromopenta-aquochromium(III) ion at 318.1 K.

$[$Complex$]$ <u>ca.</u> 0.02M $\qquad$ $[H^+] = 0.80M$

$[HNO_2] = 0.005M$ $\qquad$ $[NO_3^-] = 0.05M$
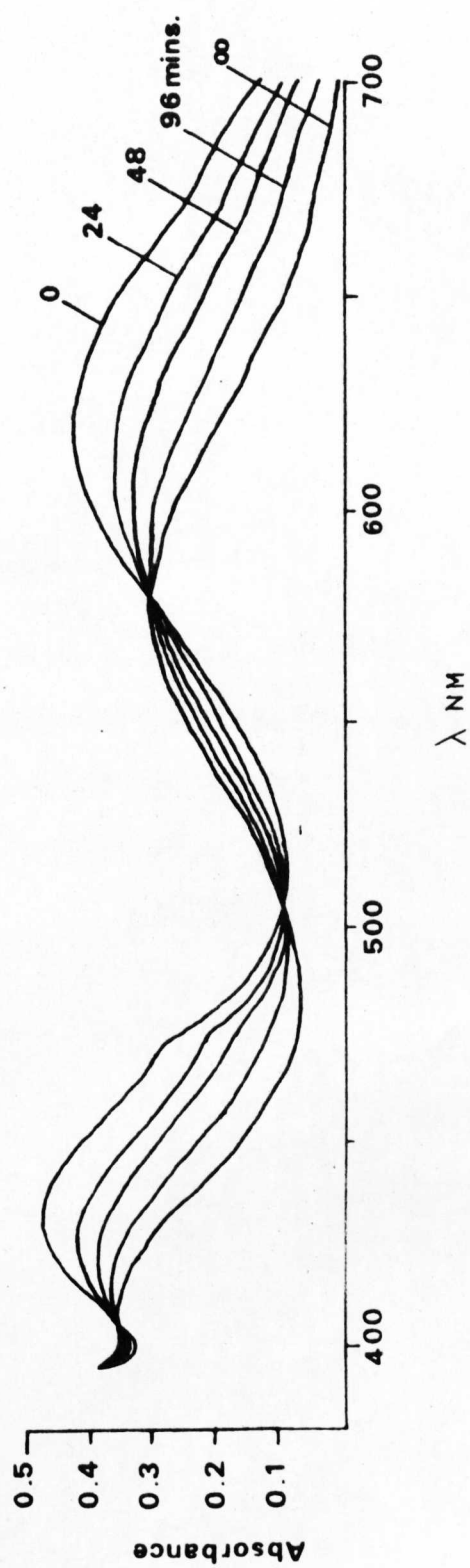
I = 1.0 $(NaClO_4)$ $\qquad$ 1 cm pathlength cell

Spectral changes (to 65% completion of reaction)

accompanying the aquation of the

cis-chloro-aquotetra-amminechromium(III) ion at 318.1 K.

[Complex] = 0.013M   [H$^+$] = 0.031M

[HNO$_2$] = 0.04M   [NO$_3^-$] = 0.05M

I = 1.0 (NaClO$_4$)   1 cm pathlength cell

ABSORBANCE

FIGURE E

Spectrum of the

trans-nitrito-aquotetra-amminechromium(III) ion

in aqueous pH 4 buffer solution at 273 K.
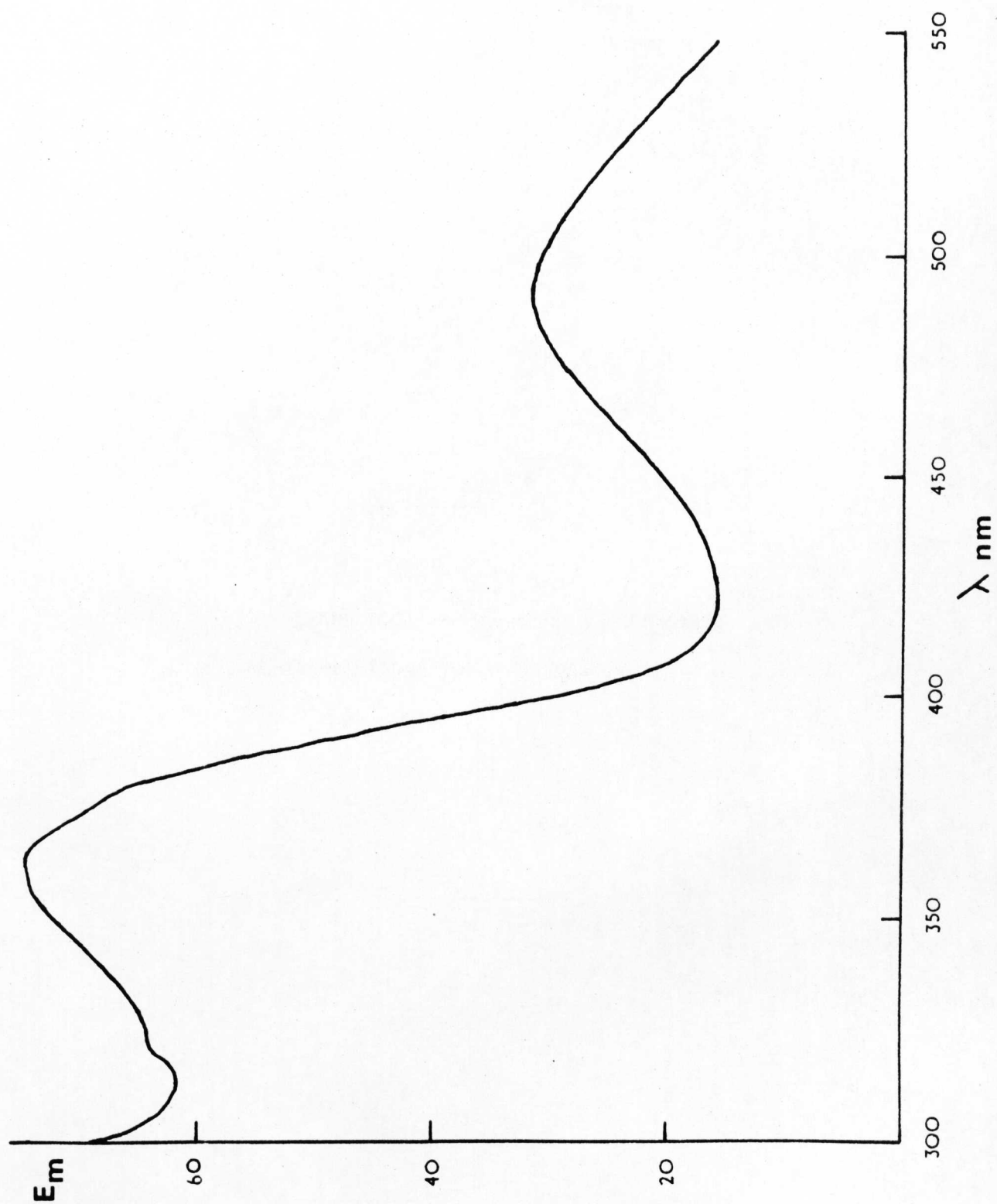
Spectrum of the

trans-chloronitritotetra-amminechromium(III) ion

in neutral aqueous solution at 283 K.

FIGURE H

Spectra of :

P   the hexa-aquochromium(III)

ion in dilute aqueous $HClO_4$

Q   the nitrite ion in

neutral aqueous solution

R   the nitritopenta-aquochromium(III) ion

in aqueous 1M $NaClO_4$ solution

at pH 3.7 and 280 K.

S   as R, but in aqueous 1M $HClO_4$

$[Complex] = 5 \times 10^{-5} M$

1 cm pathlength cell

T   as R, $[Complex] = 5 \times 10^{-5} M$

1 cm pathlength cell
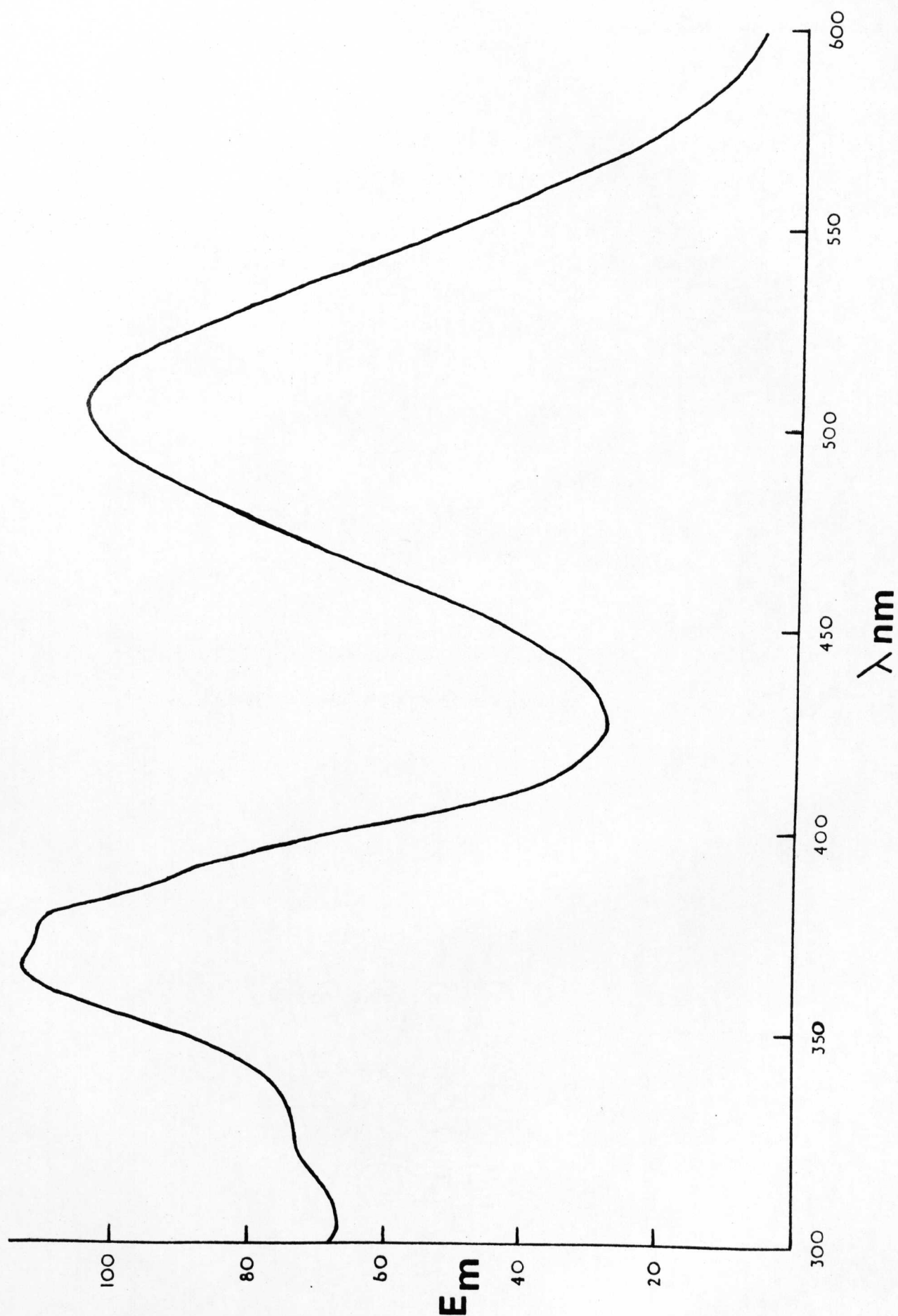
TABLE A

Résumé of I.R. Spectral Parameters

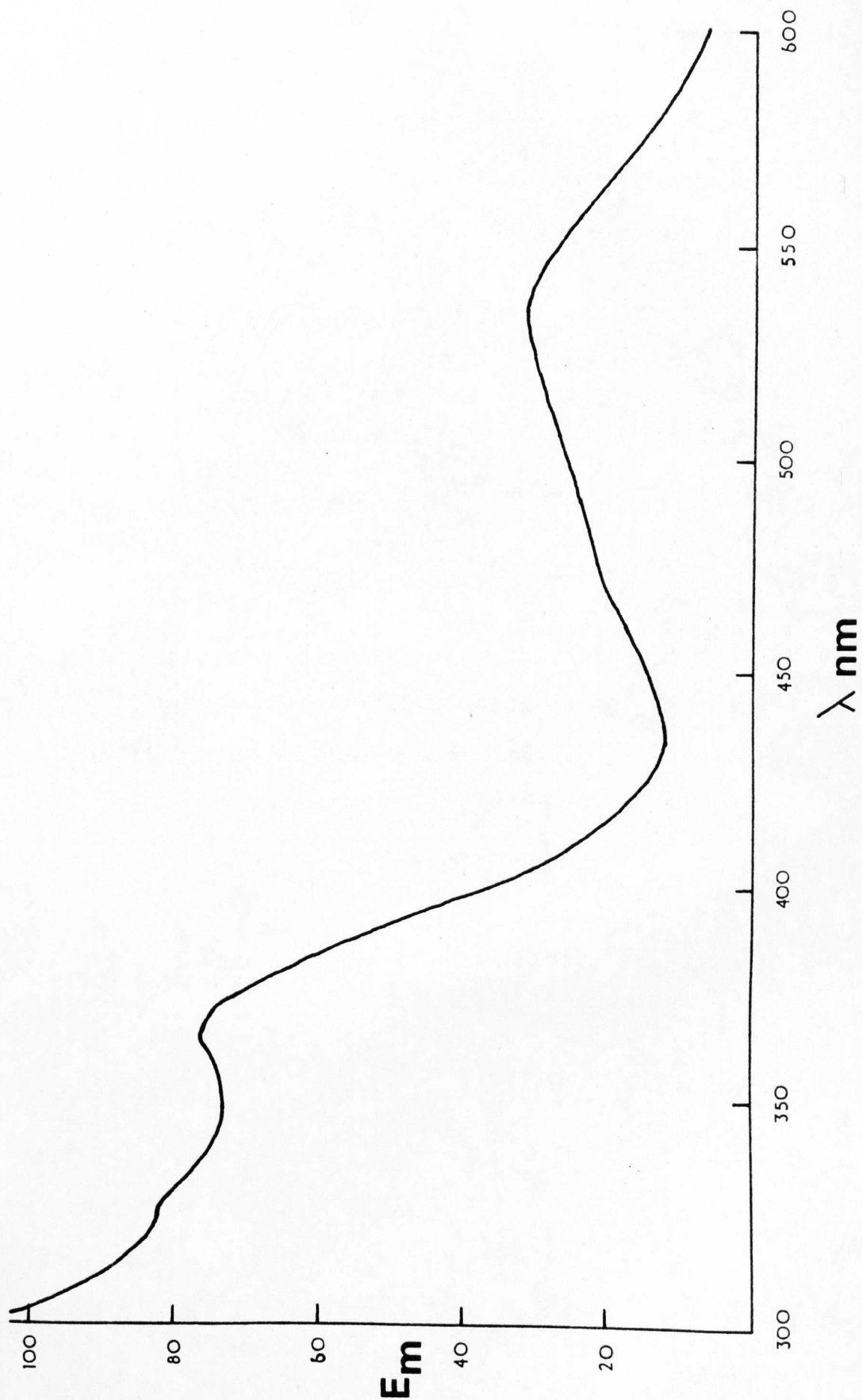| Complex	$\nu(NH_3)$	$\delta_d(NH_3)$	$\nu_{as}(ONO)$	$\delta_s(NH_3)$	$\nu_s(ONO)$	$\delta(ONO)$	$\rho_r(NH_3)$	$\nu(Cr-N)$	$\nu(Cr-O)$
NaNO₂	-	-	1325(m)	-	1270(s)	825(w)	-	-	-
[Cr(NH₃)₅H₂O](ClO₄)₃	3270(s)	1620(s)	-	1340(s)	-	-	750(s)	470(w)	-
[Cr(NH₃)₅ONO](ClO₄)₂	3290(s) 3220(w) 3160(w)	1610(m)	1470(s)	1300(s)	1040(s)	840(m)	760(m)	470(w) 444(w)	345(w)
trans-[Cr(NH₃)₄(ONO)₂]ClO₄	3340(s) 3270(s) 3190(w)	1620(s)	1470(s) 1445(s)	1310(s)	1045(s)	840(s)	745(s)	480(m) 465(w)	395(s)
cis-[Cr(NH₃)₄(ONO)₂]ClO₄	3330(s) 3270(s) 3190(w)	1615(s)	1465(s) 1440(s)	1310(s)	1020(s)	840(s)	740(s)	455(m)	360(m) 345(m)
trans-[Cr(NH₃)₄(H₂O)ONO]Cl₂	3295(s) 3150(s)	1610(m)	1430(s)	1300(s)	1030(s)	845(m)	750(s)	485(m) 465(s) 445(m)	365(m)
cis-[Cr(NH₃)₄(H₂O)ONO]Cl₂	3290(s) 3150(s)	1610(m)	1475(m)	1300(s)	1030(s)	835(m)	765(s)	475(w)	355(m)
trans-[Cr(NH₃)₄Cl(ONO)]ClO₄	3340(s) 3270(s) 3190(s)	1620(m)	1460(s)	1300(s)	1045(s)	840(m)	725(s)	480(m)	370(s)
[Co(NH₃)₅NO₂]Cl₂ [a]	-	1595	1428	1310	1310	824	850	513 499 438	-

Figures are in units of cm⁻¹. (a) From reference 145, $\rho_w(NO_2)$ is at 524 cm⁻¹.

APPENDIX 2

COMPUTER PROGRAMS

The programs listed in this appendix
are written in Elliott 4100 Algol and
were used with an Elliott 4130 computer.
The author is grateful to Dr.P.Moore
for the programs prefixed "R002" and
to Mr.D.Benton for program R026/01.

PROGRAM R001/02

RFODTD   REACTION RATES FROM OPTICAL DENSITY VERSUS TIME DATA;
"BEGIN""""INTEGER"CT,N;"REAL"Z;"READ"CT,N,Z;
"PRINT" REACTION RATES FROM O.D./T DATA L3 ;
"PRINT" S9 ,SAMELINE, OUTPUT ,DIGITS(4),CT, L3 ;
"PRINT" S4 ,SAMELINE, SECONDS , S4 , LOG(DT-DI)+3 , L2 ;
"BEGIN""""INTEGER"I;
"REAL"A,B,C,D,F,G,M,P,DM,DC,DDY,L,TR,DJ,DTR;
"ARRAY"X,Y[1:N];
A:=B:=D:=F:=G:=0;
"FOR"I:=1"STEP"1"UNTIL"N"DO""""BEGIN""""READ"X[I],Y[I];
Y[I]:=((0.4343*LN(ABS(Y[I]-Z))+3);
"PRINT" S1 ,SAMELINE,ALIGNED(6,2),X[I], S6 ,ALIGNED(1,4),Y[I], L ;
A:=A+X[I];
B:=B+X[I]*Y[I];
D:=D+Y[I];
F:=F+X[I]*X[I];
"END";
P:=N*F-A*A;
M:=(N*B-A*D)/P;
C:=(F*D-A*B)/P;
"FOR"I:=1"STEP"1"UNTIL"N"DO"G:=G+(M*X[I]+C-Y[I])↑2;
DDY:=SQRT(G/(N-2));
DM:=DDY*SQRT(N/P);
DC:=DDY*SQRT(F/P);
L:=ABS(((LN(2.0))*0.4343)/M);
TR:=(1.0/L);
DJ:=(DM*(L↑2))/0.693;
DTR:=(DJ*(TR↑2));
"PRINT" L2 ,SAMELINE, S19 , DO = ,
FREEPOINT(4),(EXP(2.303*(C-3))+Z), L2 ;
"PRINT" HALF-LIFE OF REACTION = ,SAMELINE,FREEPOINT(6),L, S , SECS,
    S9 , ERROR = ,DJ, L2 ;
"PRINT" S5 ,SAMELINE, RATE OF REACTION = ,SCALED(4),TR*0.693, S ,
 SEC-1 , S6 , ERROR = ,DTR*0.693, L5 ;
"END";
"COMMENT"INPUTS AS FOLLOWS:CT(DATA LABEL), N(NO. OF POINTS),
Z(D INFINITY),
X[1](TIME IN SECONDS), Y[1](O.D. AT TIME X[1]) ....
X[N], Y[N];
"END"OFPROGRAM;

PROGRAM R001/08


```
SP    SWINBOURNE PLOT;
"BEGIN""INTEGER"CT,N;"READ"CT,N;
"PRINT"`SWINBOURNE ESTIMATION OF D.INF.`L3``;
"PRINT"``S9``,SAMELINE,`OUTPUT`,DIGITS(4),CT,``L3``;
"BEGIN""INTEGER"I;"REAL"A,B,C,D,F,G,M,P,Z,DC,DM,DZ,DDY;
"ARRAY"X,Y[1:N];A:=B:=D:=F:=G:=0;
"FOR"I:=1"STEP"1"UNTIL"N"DO""BEGIN""READ"X[I],Y[I];
A:=A+X[I];B:=B+X[I]*Y[I];D:=D+Y[I];F:=F+X[I]*X[I];
"END";
P:=N*F-A*A;M:=(N*B-A*D)/P;C:=(F*D-A*B)/P;Z:=C/(1-M);
"FOR"I:=1"STEP"1"UNTIL"N"DO"G:=G+(M*X[I]+C-Y[I])↑2;
DDY:=SQRT(G/(N-2));DM:=DDY*SQRT(N/P);
DC:=DDY*SQRT(F/P);DZ:=C*DM/((1-M)↑2)+DC/(1-M);
"PRINT"`CALCULATED D.INF.= `,SAMELINE,Z,``S10``,`ERROR = `,DZ,``L5``;
"END";
"COMMENT" INPUTS AS FOLLOWS: CT(DATA LABEL), N(NO. OF POINTS),
DT[1],D(T+C)[1]................
DT[N],D(T+C)[N];
"END"OFPROGRAM;
```


PROGRAM R002/01


```
WLLSA  WEIGHTED LINEAR LEAST SQUARES ANALYSIS;
"BEGIN""INTEGER"CT,N;"READ"CT,N;
"PRINT"`WEIGHTED LINEAR LEAST SQUARES ANALYSIS`L3``;
"PRINT"`OUTPUT`,SAMELINE,DIGITS(4),CT,``L``;
"BEGIN""REAL"A,B,C,D,F,G,H,M,P,DM,DC,DDY;
"INTEGER"I;"ARRAY"X,Y,DY,W[1:N];
A:=B:=D:=F:=G:=H:=0;
"FOR"I:=1"STEP"1"UNTIL"N"DO""BEGIN""READ"X[I],Y[I],DY[I];
W[I]:=1/(DY[I]*DY[I]);
H:=H+W[I];A:=A+W[I]*X[I];B:=B+W[I]*X[I]*Y[I];D:=D+W[I]*Y[I];
F:=F+W[I]*X[I]*X[I];"END";
P:=H*F-A*A;M:=(H*B-A*D)/P;C:=(F*D-A*B)/P;
"FOR"I:=1"STEP"1"UNTIL"N"DO"G:=G+((M*X[I]+C-Y[I])↑2)*W[I];
DDY:=SQRT(G/(N-2));
DM:=DDY*SQRT(H/P);DC:=DDY*SQRT(F/P);
"PRINT"``S4``,SAMELINE,`C = `,C,``S6``,`ESD C = `,DC,``L``;
"PRINT"``S4``,SAMELINE,`M = `,M,``S6``,`ESD M = `,DM,``L``;
"PRINT"`ESD Y = `,SAMELINE,DDY,``L4``;  "END";
"COMMENT"INPUTS AS FOLLOWS: CT(DATA LABEL), N(NO. OF POINTS),
X[1],Y[1],ESD Y[1].....................
X[N],Y[N],ESD Y[N];
"COMMENT" IF WEIGHTING IS NOT REQUIRED SET ALL ESD Y VALUES
TO UNITY;
"END"OFPROGRAM;
```

PROGRAM R002/05

```
WLSAQD   WEIGHTED LEAST SQUARES ANALYSIS OF A QUADRATIC;
"BEGIN""INTEGER"CT,N;"READ"CT,N;
"PRINT" 'OUTPUT ',SAMELINE,DIGITS(2),CT,''L3'';
"BEGIN""REAL"A,B,C,D,F,G,H,M,P,Q,R,S,T,U,V,Z,CO,C1,C2;
"INTEGER"I;"ARRAY"X,Y,DY,W[1:N];
A:=B:=D:=F:=G:=H:=R:=S:=T:=U:=0;
"PRINT"''S5'',SAMELINE,'X'S14'','Y'S10'','WEIGHT'L2'';
"FOR"I:=1"STEP"1"UNTIL"N"DO""BEGIN""READ"X[I],Y[I],DY[I];
W[I]:=1/(DY[I]*DY[I]);
"PRINT"SCALED(6),X[I],SAMELINE,''S3'',Y[I],''S3'',W[I],''L'';
H:=H+W[I];A:=A+W[I]*X[I];B:=B+W[I]*X[I]*Y[I];D:=D+W[I]*Y[I];
F:=F+W[I]*X[I]*X[I];
S:=S+W[I]*X[I]*X[I]*X[I];
T:=T+W[I]*X[I]*X[I]*Y[I];
U:=U+W[I]*X[I]*X[I]*X[I]*X[I];"END";
P:=H*F-A*A;M:=(H*B-A*D)/P;C:=(F*D-A*B)/P;
Q:=H*(F*U-S*S)-A*(A*U-F*S)+F*(A*S-F*F);
CO:=(D*(F*U-S*S)-A*(B*U-T*S)+F*(B*S-F*T))/Q;
C1:=(H*(B*U-S*T)-D*(A*U-F*S)+F*(A*T-F*B))/Q;
C2:=(H*(F*T-B*S)-A*(A*T-F*B)+D*(A*S-F*F))/Q;
"FOR"I:=1"STEP"1"UNTIL"N"DO""BEGIN"
G:=G+((M*X[I]+C-Y[I])↑2)*W[I];
R:=R+((CO+C1*X[I]+C2*X[I]*X[I]-Y[I])↑2)*W[I];"END";
Z:=SQRT(G/(N-2));V:=SQRT(R/(N-3));
"PRINT"''L3'',SAMELINE,'LINEAR LEAST SQUARES ANALYSIS Y = M*X + C ',
  ''L3'';
"PRINT"''S4'',SAMELINE,'M = ',M,''S6'',
 'ESD M = ',Z*SQRT(H/P),''L';
"PRINT"''S4'',SAMELINE,'C = ',C,''S6'',
 'ESD C = ',Z*SQRT(F/P),''L'';
"PRINT"'ESD Y = ',SAMELINE,Z,''L3'';
"PRINT"'CURVE FITTING TO Y = C(0) + C(1)*X + C(2)*X*X'L3'';
"PRINT"''S4'',SAMELINE,'C(0) = ',CO,''S6'',
 'ESD C(0) = ',V*SQRT((F*U-S*S)/Q),''L'';
"PRINT"''S4'',SAMELINE,'C(1) = ',C1,''S6'',
 'ESD C(1) = ',V*SQRT((H*U-F*F)/Q),''L'';
"PRINT"''S4'',SAMELINE,'C(2) = ',C2,''S6'',
 'ESD C(2) = ',V*SQRT((H*F-A*A)/Q),''L'';
"PRINT"''S3'',SAMELINE,'ESD Y = ',V,''F'';"END";
"COMMENT"INPUTS AS FOLLOWS: CT(DATA LABEL), N(NO. OF POINTS),
X[1], Y[1], ESD Y[1], ...   X[N], Y[N], ESD Y[N];
IF WEIGHTING NOT REQUIRED SET ALL ESD Y VALUES
TO UNITY;
"END" OF PROGRAM;
```

PROGRAM R002/06

ACTPAR ACTIVATION PARAMETERS;
"BEGIN""INTEGER"N;"READ"N;
"PRINT"`CALCULATION OF ACTIVATION PARAMETERS FOR SYSTEM :`L9``;
"BEGIN""REAL"A,B,C,D,F,G,H,M,P,DM,DC,DDY;
"INTEGER"I;"ARRAY"X,Y,DY,W[1:N];
A:=B:=D:=F:=G:=H:=0;
"PRINT"` TEMPERATURE          RATE              WEIGHT`L``;
"PRINT"`(CENTIGRADE)        CONSTANT`L2``;
"FOR"I:=1"STEP"1"UNTIL"N"DO"
"BEGIN""READ"X[I],Y[I],DY[I];
"IF"DY[I]-1=0"THEN""GOTO"L1;
DY[I]:=DY[I]/Y[I];
L1:W[I]:=1/(DY[I]*DY[I]);
"PRINT"``S3``,SAMELINE,ALIGNED(3,1),X[I],``S7``,
SCALED(4),Y[I],``S6``,W[I],``L``;
X[I]:=1000/(273.1+X[I]);Y[I]:=LN(Y[I]);
H:=H+W[I];A:=A+W[I]*X[I];
B:=B+W[I]*X[I]*Y[I];D:=D+W[I]*Y[I];
F:=F+W[I]*X[I]*X[I];"END";
P:=H*F-A*A;M:=-(H*B-A*D)/P;C:=(F*D-A*B)/P;
"FOR"I:=1"STEP"1"UNTIL"N"DO"G:=G+((M*X[I]+C-Y[I])↑2)*W[I];
DDY:=SQRT(G/(N-2));DM:=DDY*SQRT(H/P);DC:=DDY*SQRT(F/P);
"PRINT"`L4 ARRHENIUS PARAMETERS : L2``;
"PRINT"`S2 ENERGY OF ACTIVATION = `,SAMELINE,
ALIGNED(2,2),-1.9872*M,`S4 E.S.D. = `,1.9872*DM,` KCALS. PER MOLE`;
"PRINT"`L`,SAMELINE,`S8 LOG10(A-FACTOR) = `,
ALIGNED(2,2),C/2.303,`S4 E.S.D. = `,DC/2.303,`L3``;
"PRINT"`ENTHALPY OF ACTIVATION = `,SAMELINE,
ALIGNED(2,2),-1.9872*(M+0.2981),
`S4 E.S.D. = `,1.9872*DM,` KCALS. PER MOLE AT 25 DEGREES CENTIGRADE`;
"PRINT"`L`,SAMELINE,` ENTROPY OF ACTIVATION = `,
ALIGNED(2,2),1.9872*(C-30.4575),`S4 E.S.D. = `,
1.9872*DC,` E.U.`,`S12 AT 25 DEGREES CENTIGRADE F``;"END";
"COMMENT"INPUTS AS FOLLOWS: N(NO. OF POINTS), T[1](CENTIGRADE),
K[1](RATE CONSTANT AT T[1], UNITS OF MOLES AND SECS.), E.S.D. K[1]......
T[N], K[N], E.S.D. K[N];
"COMMENT" IF EQUAL WEIGHTING OF POINTS REQUIRED SET ALL ESD K VALUES
TO UNITY;
"END" OF PROGRAM;

PROGRAM R026/01

```
S FDATA  REACTION RATES AND PLOTS FROM STOPPED-FLOW DATA;
"BEGIN"
"ARRAY"  XX, YY[0:30,0:30];
"ARRAY"AA,BB[0:30];
"ARRAY"EE[0:30];
"INTEGER"NS,J;
"INTEGER""ARRAY"N[0:30];
"INTEGER""ARRAY"CT[0:30];
"INTEGER"V;"REAL"W;
"READ" NS;
V:=50;W:=0.1;
"FOR" J:=0"STEP" 1"UNTIL" ( NS - 1) "DO"
"BEGIN""READ"CT[J],N[J];
"PRINT"``F``,`STOPPED-FLOW DATA`,``L3``;
"PRINT"`RUN NUMBER`,``S2``,SAMELINE,CT[J],``L3``;
"BEGIN""REAL"IO,INF,K,C,D,F,G,M,DY;
"REAL"A,B,E;
"INTEGER"I;
"ARRAY"T,DT,Y[0:N[J]-1];
"READ"IO,INF,K;
"PRINT"``S``,SAMELINE,`T (MSECS)     D(T)      LOG[D(T)-D(INF)] + 2`,
``L2``;
"FOR"I:=0"STEP"1"UNTIL"N[J]-1"DO"
"BEGIN""READ"T[I],DT[I];
DT[I]:=INF-DT[I];
"END";
INF:=(LN(IO/INF))/2.303;
"FOR"I:=0"STEP"1"UNTIL"N[J]-1"DO"
"BEGIN"
T[I]:=K*T[I];
XX[I,J]:=T[I];
DT[I]:=(LN(IO/DT[I]))/2.303;
Y[I]:=LN(ABS(DT[I]-INF));
YY[I,J]:=((Y[I]/2.303)+2);
"PRINT"FREEPOINT(6),T[I],SAMELINE,``S4``,DT[I],``S6``,
((Y[I]/2.303) + 2 ) ,``L``;"END" ;
"PRINT"``L``,SAMELINE,``S``,`INFINITY`S3``,FREEPOINT(6),INF,``L5``;
"COMMENT"LEAST SQUARES ANALYSIS FOLLOWS;
"PRINT"`LEAST SQUARES ANALYSIS OF DATA ABOVE`,``L2``;
A:=B:=D:=E:=G:=0;
"FOR"I:=0"STEP"1"UNTIL"N[J]-1"DO"
"BEGIN"A:=A+T[I];
B:=B+Y[I];
D:=D+T[I]*T[I];
E:=E+T[I]*Y[I];
"END"; F:=N[J]*D-A*A;
M:=(N[J]*E-A*B)/F;
C:=(B*D-A*E)/F;
EE[J]:=XX[N[J]-1,J];
"FOR"I:=1"STEP"1"UNTIL"N[J]-1"DO"
"IF"YY[I,J]<0"AND"YY[I-1,J]"GE"0"THEN"EE[J]:=XX[I,J];
"FOR"I:=0"STEP"1"UNTIL"N[J]-1"DO"
G:=G+(M*T[I]+C-Y[I])↑2;
DY:=SQRT(G/(N[J]-2));

"PRINT"``S8``,SAMELINE,`K = `,FREEPOINT(6),(-1000*M),
` SECONDS(-1)`,``S6``,`ESD K = `,
(1000*DY*SQRT(N[J]/F)),`` S SECONDS(-1)``,``L2``;
```

```
"PRINT" `HALF-LIFE = `,SAMELINE,FREEPOINT(6),
(-0.693/M), ``S MILLISECONDS``;
BB[J]:=M/2.303;
AA[J]:=C/2.303 +2;
"END";
"END";
"BEGIN"""INTEGER"M,I,MM,D,Z;
"REAL" XSCALE,YSCALE;
"REAL"QQ,LY;
"COMMENT" N = TOTAL NO. OF POINTS
V=X SCALE PLOTTER STEP
W = Y SCALE PLOTTER STEP
D=MAX VALUE OF X
E=LAST CO-ORDINATE PLOTTED;
PUNCH(5);
SETORIGIN(600,0);
XSCALE:=-1.0106;
YSCALE:=-1.0106;
LY:=1.0106;
"FOR" J:= 0 "STEP" 1 "UNTIL" (NS-1) "DO"
"BEGIN"
N[J]:=N[J]-1;
"FOR"I:=0"STEP"1"UNTIL"N[J]"DO"
"BEGIN"
"IF"YY[I,J]<LY"THEN"LY:=YY[I,J];
"IF"YY[I,J]>YSCALE"THEN"YSCALE:=YY[I,J];
"IF"XX[I,J]>XSCALE"THEN"XSCALE:=XX[I,J]    "END";
"END";
QQ:=(ENTIER(LY/W))*W;
"IF"LY<0.3"AND"LY>0.0"THEN"QQ:=0.0;
YSCALE:=YSCALE+NS*W-QQ;
"IF"XSCALE>500"THEN"V:=100;
"IF"XSCALE>1000"THEN"V:=500;
"IF"XSCALE>5000"THEN"V:=1000;
"IF"XSCALE>10000"THEN"V:=5000;
"IF"XSCALE>50000"THEN"V:=10000;
"IF"XSCALE>100000"THEN"V:=50000;
M:=ENTIER(YSCALE/W+1.0);
Z:=ENTIER(XSCALE/V+1.0);
YSCALE:=2000/W/M;
XSCALE:=1600/V/Z;
MOVEPEN(0,0);
"FOR"I:=1"STEP"1"UNTIL"Z"DO"
"BEGIN"DRAWLINE(I*XSCALE*V,0);
DRAWLINE(I*XSCALE*V,20);
DRAWLINE(I*XSCALE*V,0);
"END";
"FOR"I:=1"STEP"1"UNTIL"M"DO"
"BEGIN"DRAWLINE(1600,I*YSCALE*W);
DRAWLINE(1580,I*YSCALE*W);
DRAWLINE(1600,I*YSCALE*W);
"END";
"FOR"I:=Z-1"STEP"-1"UNTIL"0"DO"
"BEGIN"DRAWLINE(I*XSCALE*V,2000);
DRAWLINE(I*XSCALE*V,1980);
DRAWLINE(I*XSCALE*V,2000);
"END";
"FOR"I:=M-1"STEP"-1"UNTIL"0"DO"
"BEGIN"DRAWLINE(0,I*YSCALE*W);
DRAWLINE(20,I*YSCALE*W);
```

```
DRAWLINE(0,I*YSCALE *W);
"END";
"COMMENT"AXES NOW COMPLETE;
"FOR"I:=0"STEP"1"UNTIL"M"DO"
"BEGIN"
MOVEPEN(-300,I*YSCALE*W-15.0);
"PRINT"WAY(0,5),ALIGNED(3,3),(I*W+QQ);
"END";
"FOR" I:=0"STEP"1"UNTIL"Z"DO""BEGIN"
MOVEPEN(I*XSCALE*V-210,-60);
"PRINT"WAY(0,5),I*V;
"END";
MOVEPEN(200,2050);
"PRINT" WAY(0,5),`SFDATA RUN NO`;
"FOR" J:=0"STEP" 1"UNTIL" ( NS - 1) "DO"
"BEGIN"
"FOR"I:=0"STEP"1"UNTIL"N[J]"DO"
"BEGIN"MOVEPEN(XSCALE*XX[I,J], YSCALE*(YY[I,J]+J*W-QQ));
CENCHARACTER(J+1);
"END";
MOVEPEN(0,(AA[J]+J*W-QQ)*YSCALE);
DRAWLINE(EE[J]*XSCALE,(AA[J]+BB[J]*EE[J]+J*W-QQ)*YSCALE);
MOVEPEN(1300,1900-J*50);
"PRINT"WAY(0,3),ALIGNED(4,0),CT[J];
MOVEPEN(1500,1910-J*50);
CENCHARACTER(J+1);
MOVEPEN(500+150*J,2050);
"PRINT"WAY(0,5),ALIGNED(4,0),CT[J];
"END";
MOVEPEN(-330,600);
"PRINT"WAY(1,5),`LOG[D(T)-D(INF)]+2`;
MOVEPEN(750,-200);
"PRINT" WAY(0,5),`TIME (MSECS)`;
MOVEPEN(0,3500);
"END";
"COMMENT" INPUTS AS FOLLOWS:  "&RUN" CARD, M(NO. OF LINES TO BE PLOTTED
PER SET OF AXES, MAX OF 8), CT[A](DATA LABEL OF FIRST PLOT),
N[A](NO. OF POINTS IN PLOT "A"), I0[A](100% TRANSMISSION),
INF[A](INFINITY READING), K[A](TIME FACTOR, 1 MM = K MS),
T[1A](TIME IN MM), I[1A](INTENSITY AT TIME T[1A]).......T[NA], I[NA],
CT[B], N[B], ETC........CT[M], N[M], ETC........
CONTROL CARD;
"END"OFPROGRAM;
```

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