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VOLUME PARAMETERS IN MECHANISTIC STUDIES OF TRANSITION METAL COMPLEX IONS IN SOLUTION

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "VOLUME PARAMETERS IN MECHANISTIC STUDIES OF TRANSITION METAL COMPLEX IONS IN SOLUTION" submitted by Margaret Joy Sisley in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

The effects of changes in temperature and pressure on the rate of exchange of solvent with $Rh(NH_3)_5DMF^{3+}$ in DMF (N,N-dimethylformamide) have been investigated. The values of the activation parameters were found to be: $\Delta H^* = 99.1 \pm 2.0$ kJ mol^{-1}, $\Delta S^* = -19.8 \pm 6.0$ J K^{-1} mol^{-1}, and $\Delta V^* = -1.4 \pm 0.2$ cm^3 mol^{-1}. The negative, pressure-independent ΔV^* is interpreted in terms of an associative interchange mechanism. Attempts have been made to measure the enthalpy of activation for anation of $Rh(NH_3)_5DMF^{3+}$ by Cl^-, Br^- and NCS^-, but all efforts failed due to the precipitation of the complex ions involved.

The anation of $Cr(DMF)_6{}^{3+}$ by Br^- in DMF has proved to be a reversible reaction, with the reaction being 98% complete at 0.1 MPa, but only 30% complete at 400 MPa, when $[Br^-] = 7.90 \times 10^{-2}$ m and T = 85°C. Using the volume of reaction, which is effectively constant over the range of pressures studied, the observed rate coefficients for the approach to equilibrium were separated into the anation and solvolysis components. The $\Delta V_0{}^*$ values for the anation and solvolysis processes have been found to be $+13 \pm 2$ cm^3 mol^{-1} (pressure-dependent) and approximately -20 cm^3 mol^{-1} (slightly pressure-dependent) at 85°C. The values of ΔV_{IP} and ΔV have also been determined, being about 0 cm^3 mol^{-1} and +35.3 cm^3 mol^{-1}, respectively. These results are found to be consistent with the operation of an I_a mechanism. In contrast to what is observed in most aqueous systems, the degree of solvational change throughout the reaction process is very small. The observed volume changes are large, however, because of the larger molar volume of DMF relative to water.

The effect of temperature on the volumes of activation for the spontaneous and acid-catalysed aquation pathways of $Co(NH_3)_5SO_4^+$ has been studied. The volumes of activation for the spontaneous pathway at 35 and 55°C have been found to be -18.3±0.4 and -19.7±0.8 $cm^3\ mol^{-1}$ (pressure-dependent), while those for the acid-catalysed path are -3.5±0.6 and -3.9±0.5 $cm^3\ mol^{-1}$ (pressure-independent). The temperature-dependence of ΔV_0^* for the uncatalysed path could be accounted for on the basis of the thermal expansivity of the solvent molecules gained by the reactants on going to the transition state. The ΔV^* values for the acid-catalysed path were less negative than those for the uncatalysed path by an amount corresponding to the difference in volume between the HSO_4^- and SO_4^{2-} leaving groups, indicating that the rate-determining steps for the two processes proceed by similar mechanisms.

The partial molal volumes of some acidopentaammine-cobalt(III) and chromium(III) complexes were re-determined. The results suggest that the values found for some of the cobalt complexes by Palmer and Kelm[19] were too high, apparently because of the presence of adsorbed $HClO_4$ on the surface of the solid compounds.

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LIST OF ABBREVIATIONS

A	associative mechanism
c	concentration (mol L^{-1} unless otherwise stated)
d	density (g cm^3)
D	dissociative mechanism
D_{cb}	dissociative conjugate base mechanism
DMF	N,N-dimethylformamide
DMF-d_7	perdeuterated N,N-dimethylformamide
DMSO	dimethylsulphoxide
DMSO-d_6	perdeuterated dimethylsulphoxide
en	ethylenediamine
ΔG°	free energy of reaction
ΔG^*	free energy of activation
ΔH°	enthalpy of reaction
ΔH_{ex}^*	enthalpy of activation for solvent exchange
ΔH_i^*	enthalpy of activation for interchange
I	interchange mechanism
I_a	associative interchange mechanism
I_d	dissociative interchange mechanism
k	rate coefficient
k_{an}	anation rate coefficient
k_{aq}	aquation rate coefficient
k_{ex}	solvent exchange rate coefficient
k_i	interchange rate coefficient
k_o	rate coefficient at zero pressure
k_{obs}	observed rate coefficient
K	equilibrium constant
LFER	linear free energy relationship
LFSE	ligand field stabilisation energy
m	molality (mol kg^{-1})
m/e	mass to charge ratio
M	molarity (mol L^{-1})
MHz	megahertz
MPa	megapascal (10^6 N m^{-2})
NMR	nuclear magnetic resonance spectroscopy
ppm	parts per million
R	gas constant (8.3143 N m K^{-1} mol^{-1})
ΔS°	entropy of reaction
ΔS_{ex}^*	entropy of activation for solvent exchange
ΔS_i^*	entropy of activation for interchange
S_N1	substitution nucleophilic unimolecular
S_N2	substitution nucleophilic bimolecular
t	time
T	temperature (degrees Kelvin unless otherwise stated)
$\bar{V}^0$	partial molal volume
ΔV^0, ΔV	volume of reaction
ΔV_b	component of volume of reaction arising from intrinsic volumes of species involved
ΔV_{IP}	volume change on ion-pairing

ΔV_s	solvational component of volume of reaction
ΔV^*	volume of activation
ΔV_b^*	bond-making or breaking contribution to volume of activation
ΔV_0^*	volume of activation at zero pressure
ΔV_s^*	solvational contribution to volume of activation
$(\Delta V_i^*)_0$	volume of activation at zero pressure for ith reaction
x	the increase in the number of solvent molecules solvating a complex as it goes from the initial state to the transition state (from modified Tait expression)
ε	molar absorptivity (L mol^{-1} cm^{-1})
λ	wavelength
π	empirical parameter (modified Tait expression)
ρ	empirical parameter (modified Tait expression)
τ	chemical shift scale (NMR) in which tetramethylsilane is assigned a shift of 10.0 ppm
ϕ	apparent molal volume
$[X^{n-}]$	concentration of X^{n-}
{ , }	ion pair

CHAPTER I

INTRODUCTION

While reports of kinetic studies on substitution reactions of transition metal complex ions in solution have appeared in the literature for several decades, there has been an upsurge in this area during the last twenty to twenty-five years. The main purpose for these studies has been to gain information about how and why particular types of complexes react as they do. Attempts have been made to systematize the data obtained by means of general mechanisms. Once a large amount of data has been gathered as to which complexes react by which type of mechanism, it should be possible to determine what factors govern the mode of reaction in a given instance. Thus a better understanding of the chemistries of the various transition metals should be attained. Unfortunately, neither the formulation of meaningful mechanistic models nor their assignment to particular reactions is a simple matter.

1. Classification of Mechanisms

Prior to the late nineteen-sixties, inorganic chemists generally discussed the mechanisms of complex ion reactions in terms of the S_N1/S_N2 classification devised by Ingold[1] for organic reactions. Although some reactions can be discussed quite well in these terms, the majority of complex ion substitution reactions seem to fall into an intermediate region where the concepts of unimolecularity and bimolecularity are no longer clearly defined.

Basolo and Pearson[2] extended the Ingold scheme in an attempt to deal with this intermediate region. Mechanisms were defined as being S_N1 (limiting) if the rate determining step was clearly unimolecular, and

S_N2 (lim) if it was obviously bimolecular. The reaction mechanisms which lay in between were designated S_N1 or S_N2 depending upon the extent to which the entering ligand participated in the rate determining step.

Langford and Gray[3] subsequently proposed a system of classification which, while being similar to that of Basolo and Pearson in its general outline, removed the emphasis on molecularity which was one of the chief disadvantages of the older terminology. In the Langford-Gray system of nomenclature three main categories of mechanism were defined: associative (A), dissociative (D), and interchange (I).

An A-type mechanism (essentially S_N2 (lim)) involves the attack of the incoming ligand on the central metal ion, resulting in an intermediate of increased coordination number. Conversely, a D-type mechanism (S_N1 (lim)) is initiated by loss of the outgoing ligand from the metal centre, leaving an intermediate of reduced coordination number. The I-mechanism is essentially a concerted pathway in which the leaving ligand moves from the first coordination sphere of the central metal ion to the second, while the incoming ligand does the reverse. In this definition of the I-mechanism, the key point is that no intermediate is formed in which the primary coordination number of the metal centre has changed.

The I-mechanism in this system of nomenclature is further divided into associative interchange (I_a) and dissociative interchange (I_d) mechanisms. As originally defined, an I_a mechanism is much more sensitive to the nature of the entering ligand than to that of the departing one, while for an I_d mechanism the reverse is true. The I_a mechanism clearly corresponds to the S_N2 mechanism of Basolo and Pearson. The I_d mechanism is usually identified as being S_N1, but the latter term is somewhat misleading in that stoichiometrically such a reaction is bimolecular,

even though the "intimate"[3] mechanism is essentially unimolecular. The Langford-Gray terminology has been adopted by most inorganic kineticists to avoid this ambiguity.

Swaddle[4] has given more precise definitions for the various mechanisms. For substitution occurring at an approximately octahedral centre as given in equation 1, a D-type mechanism is said to be in operation if

$$ML_5X + Y \longrightarrow ML_5Y + X \qquad 1$$

the ligand X departs independently of the entry of ligand Y, leaving a five-coordinate intermediate which is long-lived relative to the relaxation time of the second coordination sphere. An A-type mechanism involves formation of a similarly long-lived seven-coordinate intermediate through attack of Y at the metal centre while X is still in the first coordination sphere. In an I-mechanism, the starting complex and entering ligand form an "encounter complex" (often an ion-pair), within which exchange of X and Y occurs on a timescale that is short relative to that for relaxation of the second coordination sphere. If the mechanism is I_d, formation of the M-Y bond begins after breaking of the M-X bond has occurred, but while X is still in the second coordination sphere. On the other hand, in an I_a mechanism the two processes are essentially synchronous.

Obviously for a reaction having an intermediate the lifetime of which is on the same timescale as the relaxation of the second coordination sphere, the distinction between A and I_a or D and I_d is no longer clear. Such regions of uncertainty are likely to exist in any classification scheme one might choose, and presumably is a reflection of the artificiality of the models. Notwithstanding this artificiality, it is convenient to employ some such terminology in dealing with reaction mech-

anisms. In the following discussion, the nomenclature of Langford and Gray as revised by Swaddle will be used.

2. A- and D-type Mechanisms

Most of the work to be described here deals with systems reacting via interchange mechanisms. Indeed, most six-coordinate cationic complexes seem to undergo substitution by routes of that type. Nevertheless, several significant examples of D- and A-type mechanisms have been reported.

D-mechanisms have been found to occur in at least four situations:

(1) When the complex ion is anionic. On purely electrostatic grounds, neither an anionic ligand nor the negative end of a neutral dipolar molecule such as water would be likely to interact with an anionic complex in an associative way. Substitution reactions of $Co^{III}(CN)_5X^{m-}$ [5] and of $Rh^{III}Cl_{6-n}OH_{2n}{}^{m-}$ (n = 0, 1, 2)[6,7] are examples of this type.

(2) When a ligand trans to the leaving group exerts a strong labilising effect. This seems to occur for complexes of the type trans-$M(en)_2X(OH_2)^{2+}$ (M = Co(III), Rh(III); X = Cl^-, Br^-, OH^-, etc.)[8], and $Rh(H_2O)_nCl_{6-n}{}^{m+}$ (n = 3, 4, 5)[6,9]. While for Co(III) the labilisation is likely due to both σ- and π-bonding effects for Rh(III) σ-bonding apparently plays the major role[8].

(3) When a conjugate base (D_{cb}) mechanism is operating. Such is the case in base hydrolyses of complexes having at least one ligand with an ionisable proton. The mechanism is described by reactions 2 through 5.

$$M(LH)L_4'X^{n+} + OH^- \rightleftharpoons MLL_4'X^{(n-1)+} + H_2O \qquad 2$$

$$MLL_4'X^{(n-1)+} \longrightarrow MLL_4'^{n+} + X^- \qquad 3$$

$$MLL_4'^{n+} + H_2O \longrightarrow MLL_4'OH_2{}^{n+} \qquad 4$$

$$MLL_4'OH_2{}^{n+} \longrightarrow M(LH)L_4'OH^{(n-1)+} \qquad 5$$

This mechanism has been most studied for the pentaamminecobalt(III) series of complexes[10], but also occurs for base hydrolysis at several other metal centres including chromium(III), ruthenium(III), and rhodium(III). In most cases, the ligand deprotonated seems to be that which is trans to the departing ligand, and thus the D_{cb} mechanism may be regarded as a special case of the trans-labilisation described in (2).

(4) When the leaving ligand cannot be retained in the second co-ordination sphere. This would be the case in metal-assisted aquations of cationic complex ions in which the departing group (for example $HgCl^+$) is of the same charge-type as the complex ion fragment remaining (perhaps $Co(NH_3)_5{}^{3+}$).

Substitution reactions proceeding by A-mechanisms are not particularly common for octahedral complex ions. Exceptions to this are the reactions of ruthenium(III) complexes, including that given in equation 6[11].

$$Ru(NH_3)_5Cl^{2+} + H_2O \rightleftharpoons Ru(NH_3)_5OH_2{}^{3+} + Cl^- \qquad 6$$

The occurrence of such mechanisms for ruthenium(III) may be explained, at least in part, in terms of the occupancy of the metal 4d orbitals[12]. Ruthenium(III) is a t_{2g}^5 ion, and hence has a vacancy in a non-bonding orbital which can accommodate electron density from a seventh ligand without being unduly destabilised. This is in contrast to cobalt(III) and rhodium(III), for which the additional electron density would have to enter higher energy anti-bonding orbitals.

3. Methods for Distinguishing Between I_a and I_d Mechanisms

Apart from special cases such as those already mentioned, which are to some extent predictable, most substitution reactions of octahedral complex metal ions appear to proceed by way of interchange mechanisms.

One of the chief tasks of the inorganic kineticist has, therefore, been to devise methods for distinguishing between I_a and I_d mechanisms. With time it has become increasingly clear that the procuring of unequivocal evidence for the occurrence of one or the other in a given situation can be difficult. Several approaches have been taken with varying degrees of success.

Equations 7 and 8 represent the steps occurring in a typical interchange process.

$$ML_5S^{3+} + X^- \overset{K}{\rightleftharpoons} \{ML_5S^{3+}, X^-\} \qquad 7$$

$$\{ML_5S^{3+}, X^-\} \xrightarrow{k_i} ML_5X^{2+} + S \qquad 8$$

For the anation process as shown here, the values of k_i obtained for a variety of nucleophiles X^- reacting with the same complex would be expected to vary considerably if bond-making were the more important process (I_a), but to remain essentially constant if breaking of the metal-solvent bond were rate-determining (I_d). The reverse would be true for a solvolysis reaction. Furthermore, for an I_d anation, the values of k_i would be predicted to be less than, or perhaps equal to, the rate coefficient k_{ex} for solvent exchange (equation 9), because breaking of the

$$ML_5S^{3+} + S^* \xrightarrow{k_{ex}} ML_5S^{*3+} + S \qquad 9$$

same bond would be rate-determining in each case. For an I_a process, however, k_i could exceed k_{ex}.

For aqueous systems this method of distinguishing between I_a and I_d mechanisms has apparently worked well. In the anation of $[Co(NH_3)_5OH_2]^{3+}$ in water by a variety of nucleophiles, the rate coefficients are all within a factor of two of each other[4a] and none of the k_i's exceeds k_{ex}.

This has been taken as a clear indication of the operation of an I_d mechanism. Monacelli[13] has shown that for anation of the analogous rhodium(III) complex, k_i is greater than k_{ex} by a factor of 2.5 when $X^- = Cl^-$ and 4.9 when $X^- = Br^-$, suggesting an I_a process. Insufficient data is available for this rhodium system to show any great variation in k_i with nucleophile, but for the anations of $Cr(H_2O)_6{}^{3+}$ the rate coefficients are found to span a range of at least 10^4.[12]

Recent work by Swaddle and co-workers[14,15] has shown that k_i need not be less than k_{ex} for an I_d process occurring in a nonaqueous solvent. Anation of $Co(NH_3)_5DMSO^{3+}$ by Cl^- and Br^- in dimethylsulphoxide (DMSO) and of $Co(NH_3)_5DMF^{3+}$ by Br^- in N,N-dimethylformamide (DMF) all have values of k_i which are larger than their respective k_{ex}'s at the same temperature. This has been attributed to the bulkiness of the solvent molecules, which hinders their ability to move freely into or away from the reaction site. The observed k_{ex} is no longer a direct measure of the rate of metal-solvent bond-breaking, since often the metal will recombine with the same solvent molecule to which it was previously attached. Because of their much smaller sizes, entering groups such as Cl^- or Br^- can move into the reaction site with relative ease.

The above approach suffers from at least two other disadvantages. First, data on solvent exchange and a minimum of two to three anation or solvolysis reactions for a given complex are necessary in order to establish the mechanism. More importantly, as pointed out by Pavelich _et. al._,[16] the rate coefficients measured at high ionic strengths (> 0.3 _M_), as is the case for most anation and solvolysis reactions, are likely composite rate constants, and, therefore, may not be directly comparable with one another. This arises at least in part from ion-pairing of the reacting

complex with the anion of the supporting, supposedly inert, electrolyte used to bring the solution up to the desired ionic strength.

Instead of comparing rate coefficients directly, many authors have instead compared the values of the activation parameters derived from the temperature-dependence of these coefficients. For example, whereas comparisons of k_i with k_{ex} in nonaqueous solvents have been shown to be unsatisfactory as discussed above, the enthalpies of activation ΔH_i^* and ΔH_{ex}^* for the two processes do serve as mechanistic indicators. Because the enthalpy of activation for an I_d process reflects the energy involved in the rate-determining bond-breaking, and is not affected by any tendency of the complex to recombine with its own leaving group, ΔH_i^* should be equal to ΔH_{ex}^*. For an I_a process, bond-making by the entering ligand makes the major contribution to ΔH^*, and therefore ΔH_i^* would be expected to vary from one attacking ligand to another, and also to be different from ΔH_{ex}^*. For $Co(NH_3)_5DMSO^{3+}$ in DMSO, $\Delta H_{ex}^* = 123\pm2$ kJ mol^{-1}, while $\Delta H_i^* = 121\pm3$ kJ mol^{-1} when the anating ion is Br^- and approximately 126 kJ mol^{-1} when it is Cl^-.[14] Since <u>both</u> ΔH_i^* values are the same as ΔH_{ex}^*, the operation of an I_d mechanism seems likely. In contrast, the ΔH_i^* values for the anation of $Cr(DMF)_6{}^{3+}$ in DMF by various nucleophiles vary from at least 97 kJ mol^{-1} to 131 kJ mol^{-1}, with ΔH_{ex}^* being 97 kJ mol^{-1}, suggesting an I_a mechanism for this system[17].

Unfortunately, the values of ΔH^* (and ΔS^*) reported by different workers for the same reaction, sometimes vary to a greater extent than do values reported by a single group for a series of different reactions. Hence this approach is best used only in conjunction with other methods for determining mechanism.

Entropies of activation are rather more difficult to interpret than

are enthalpies. In general, reactions involving stereochemical change or reactants of opposite charge in the rate-determining step will have more positive entropies of activation than will reactions which are stereoretentive, or involve charged species of like sign. In other words, a more positive ΔS^* is associated with a release of solvent in going to the transition state. I_a processes are almost always stereoretentive, whereas their I_d counterparts are often accompanied by stereochemical change. On this basis alone, it might be expected that the two types of mechanism could be distinguished from one another by comparison of the ΔS^* values, at least in the case of reactions involving closely similar complex ions.

The reactions of $Cr(NH_3)_5X^{2+}$ in water are widely[18,19,20], although not universally,[21] believed to proceed by I_a mechanisms, whereas the analogous cobalt(III) complexes react via I_d routes. In spite of this, the ΔS^* values for aquation of most of the complexes in the two series are very similar (Table 1). This is in large part due to the fact that the acidopentaamminecobalt(III) complexes are stereoretentive in their aquation reactions. In addition, the transition state in an I_d process more closely resembles the products than does that for an I_a process. Consequently, the increased solvation expected on going from a doubly charged reactant to a triply positive product and a minus one product will make a larger negative contribution to ΔS^* in an I_d process. In any case, it is clear that an assignment of mechanism based only on ΔS^* is impossible.

One approach to mechanistic studies which has enjoyed some success, but which has the disadvantage of requiring a fairly large amount of data, is the use of linear free energy relationships (LFER). For octahedral substitution reactions the discussion has centred mainly around LFER which compare kinetic and thermodynamic properties such as ln k <u>versus</u>

Table 1. Entropies of Activation[≠] for the Aquation of $M(NH_3)_5X^{2+}$

Complex	ΔS^* (J deg^{-1} mol^{-1})
$Co(NH_3)_5F^{2+}$	-37.3
$Cr(NH_3)_5F^{2+}$	-26.8
$Co(NH_3)_5Cl^{2+}$	-28.5
$Cr(NH_3)_5Cl^{2+}$	-36.4
$Co(NH_3)_5Br^{2+}$	-15.9
$Cr(NH_3)_5Br^{2+}$	-15.1
$Co(NH_3)_5NCS^{2+}$	-3.4
$Cr(NH_3)_5NCS^{2+}$	-34.8

≠ Values taken from Reference 22

ln K or ΔG^* versus $\Delta G°$, and around other types of relationships arising from the free energy correlations (ΔH^* versus $\Delta H°$, ΔS^* versus $\Delta S°$, and the like)[3,4a]. For reactions in which the transition state resembles the products, as in an I_d mechanism, a straight line with a slope of about 1.0 should be obtained in a plot of the kinetic parameter against the thermodynamic one. Such was found to be the case in a plot of ln k versus ln K for the aquation of several $Co(NH_3)_5X^{2+}$ ions[23]. For reactions other than those in which the transition state is essentially product-like, nonlinear ΔG^* vs $\Delta G°$ plots would be expected. If, however, the range of $\Delta G°$ values for the series of reactions under consideration is quite limited, a plot that is linear within the experimental error will be obtained[4a]. For slow I_a processes this seems to be the case, with slopes in the region of 0.5 being obtained. The aquation of various $(H_2O)_5CrX^{2+}$ species is a case in point[24].

Unfortunately there are comparatively few systems for which there is sufficient data available to allow the application of LFER. Furthermore, in the case of plots based upon enthalpies or entropies, the large variation in activation parameters obtained by different groups, which was mentioned earlier, makes the choice of the appropriate values difficult. Thus LFER have not been used as extensively in mechanistic studies as they might otherwise have been.

The approaches discussed so far, especially if used together, can often be quite successful in distinguishing between the various types of reaction mechanism. As has been indicated, however, there are certain drawbacks associated with these methods. The use of volumes of activation ΔV^*, sometimes in conjunction with volumes of reaction $\Delta V°$, as an indicator of mechanistic type has proved to be an effective means of circumventing some of these problems.

4. Volumes of Reaction and Activation

The volume of reaction is defined as being the change in partial molal volume which occurs on going from the initial state to the final state. (For a reaction proceeding by an interchange mechanism, the initial state would be the encounter complex (ion-pair) rather than the reactants.) This is a thermodynamic parameter, and reflects the change in the equilibrium constant of the reaction with pressure (equation 10).

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = \left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = -\frac{\Delta V^\circ}{RT} \qquad 10$$

In practise, ΔV° is usually measured directly by dilatometry[25] or densimetry[11], or is calculated from the apparent molal volumes ϕ_V of the reactants and products (equation 11)[19].

$$\Delta V^\circ = \Sigma\phi_{v(\text{products})} - \Sigma\phi_{v(\text{reactants})} \qquad 11$$

Similarly, the volume of activation is the change in partial molal volume on going from the initial state to the transition state. ΔV^* can be determined by measuring the pressure-dependence of the rate coefficient for the reaction of interest (equation 12).

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \left(\frac{\partial \Delta G^*}{\partial P}\right)_T = -\frac{\Delta V^*}{RT} \qquad 12$$

In principle, it is possible to measure the volume changes occurring at each stage in a reaction mechanism (formation of the ion-pair, ion-pair going to the transition state, transition state going to products). Furthermore, since volumes, unlike entropies, are readily interpretable

in physical terms, it is possible to rationalise the observed changes in terms of the various mechanistic models proposed earlier.

Volumes of reaction are generally considered as being made up of two components (equation 13), one arising from the difference in the intrinsic volumes of the products relative to the reactants (ΔV_b) and one arising from the accompanying solvational changes (ΔV_s).

$$\Delta V^\circ = \Delta V_b + \Delta V_s \qquad 13$$

In just the same way, the volume of activation is partially the result of the volume change occurring upon the making or breaking of the bond to the incoming or outgoing group and partially a result of solvational changes.

The simplest type of reaction to consider is a solvent exchange reaction. Since the reactants and products are identical in such a case, ΔV° is equal to zero. Furthermore, if the reaction proceeds by an interchange mechanism, the activation process is rapid relative to the relaxation time of the second coordination sphere, and ΔV_s^* is usually negligible. If a metal centre and the ligands coordinated octahedrally to it are envisaged as constituting an essentially spherical entity[26] in the solution, it might be expected that the loss or gain of a ligand would not appreciably alter the volume occupied by the metal and its other ligands (figure 1). Thus the observed volume of activation would be a result of increases or decreases in volume occurring outside of the spherical volume defined by the first coordination sphere. This model is in fact an oversimplification. When a metal centre undergoes a reduction in its coordination number, the bonds to its remaining ligands become stronger and shorter. If an increase in coordination number

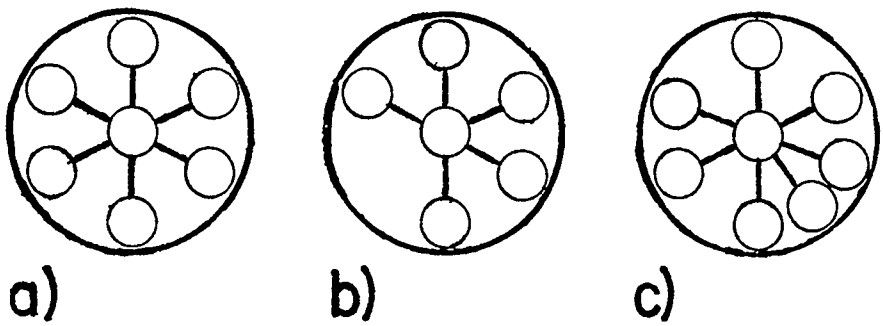


Figure 1. Spherical volume occupied by a) octahedral complex b) five-coordinate intermediate c) seven-coordinate intermediate

occurs, the bonds to the original ligands then become weaker and longer[27]. Loss of a ligand from the first coordination sphere will result in an increase in volume on going to the transition state which is partially, but not wholly, compensated for by the decrease in bond-lengths between the metal centre and its non-reacting ligands. The net result will be a volume of activation of positive sign. This is the case in an I_d or D mechanism. Conversely, an I_a or A mechanism would involve the entry of a seventh ligand into the first coordination sphere, with a net decrease in volume on formation of the activated complex. An associatively activated process would therefore have a negative volume of activation. In experimental terms, as can be seen in equation 12 or predicted by means of Le Châtelier's Principle, a positive ΔV^* is manifested by a decrease in rate coefficient with increasing pressure, while for a negative ΔV^* increasing

pressure causes an increase in the rate coefficient of the reaction. Thus it is possible to distinguish between associatively and dissociatively activated solvent exchange reactions on the basis of the sign of ΔV^*.

Whereas $\Delta V_s^* \approx 0$ for most I_a and I_d solvent exchange reactions, this is not the case for D and A reactions. Because the intermediates are long-lived relative to the relaxation time of the second coordination sphere, considerable rearrangement of a solvational nature and of the non-reacting ligands can occur within the time-span of the activation process. These rearrangements will involve bulk solvent as well as solvent in the first and second coordination spheres. By virtue of the strong electrostatic attraction existing between a central metal and the solvent in the first and second coordination spheres, that solvent is virtually incompressible. Consequently, any exchange of solvent between the two coordination spheres should result in the same volume change regardless of the external pressure (at least up to 400 MPa)[4b]. If, on the other hand, an exchange were to occur between bulk solvent and the coordination spheres, a pressure-dependent volume change would be anticipated, because the bulk solvent is highly compressible at pressures near atmospheric, but as incompressible as the coordinated solvent at very high pressures. For D- and A-type mechanisms, the absolute value of ΔV^* will thus decrease with increasing pressure, while a ΔV^* which is essentially constant will be obtained for most I_a or I_d mechanisms. Merbach and co-workers[28], however, have found that for solvent exchange by labile metal(II) species in several nonaqueous solvents, the ΔV^*'s obtained may be very slightly pressure-dependent, even though the reactions are apparently of the interchange type. It may be that the compressibility difference between the first and second coordination spheres, which is insignificant for metal(III) centres up to at least 400 MPa, is detectable at much lower

pressures in the case of metal(II) centres due to the smaller charge to radius ratios of the latter. In other words, the electrostatic force of attraction of the metal for its ligands and solvation sheaths, decreases much more rapidly with increasing distance from the metal in the case of a metal(II) centre than is the case for a metal in the plus three oxidation state. Presumably if higher pressures were used in studies of metal(III) centres, curvature of the ln k _versus_ pressure plots would be detected for these too.

So far only the relatively straightforward solvent exchange reactions have been discussed. In solvolysis and anation studies the occurrence of large solvational changes can make the interpretation of volumes of activation much less simple. For some of these reactions, the solvational contribution to ΔV^* is greater than the bonding contribution. If on going from the initial state to the transition state in a reaction charged species are neutralised, then polar solvent molecules will be released from the solvation sheaths of the reactants. This process will make a positive contribution to ΔV^*. In contrast, if the separation of opposite charges occurs, solvent electrostriction will increase and a negative contribution will be made. From this it can be seen that the ΔV_s^* component may either reinforce the ΔV_b^* component of ΔV^*, or cancel out all or part of it. Therefore, the sign associated with ΔV^* for a reaction involving marked solvational change is no longer diagnostic of the mode of activation. Furthermore, since the solvational changes brought about by the alteration in charge distribution involve bulk solvent, ΔV^* may be highly pressure-dependent, even when interchange mechanisms are in effect.

It should not be supposed from this that volume of activation

measurements are useful only in the study of solvent exchange reactions. Estimates of the size of the solvational contribution can be made by comparison of the observed ΔV^* value with that for solvent exchange in the same system[17] or by examining the solvational contribution in other reactions involving the same charge types. For dissociatively activated reactions, it may be possible to estimate ΔV_s^* on the basis of the Born theory[29], since the solvational changes will be nearly complete by the time the transition state is reached. Once allowance has been made for the ΔV_s^* contribution, the sign of the remaining ΔV_b^* is indicative of mechanism in the same way as it was for solvent exchange.

If sufficient information is available on closely related reactions, it should be possible to distinguish between I_a and I_d mechanisms without first correcting for the solvational contribution. Just as linear relationships involving ΔH^* and $\Delta H°$ or ΔS^* and $\Delta S°$ will have slopes of 1.0 or approximately 0.5 for I_d and I_a mechanisms respectively, so too will plots of ΔV^* against $\Delta V°$.[4a]

It appears that the functional dependence of ΔV^* on pressure for I_a and I_d mechanisms is different from that for A and D mechanisms[11], so that even though non-linear ln k <u>versus</u> pressure plots may be found in all cases, it may still be a relatively simple matter to distinguish I_a from A or I_d from D mechanisms. This point will be discussed more fully in chapter 3.

The use of volume measurements as diagnostic tools in mechanistic studies has some advantages over the more traditional approaches mentioned earlier. Firstly, although additional information may be gained by comparing the volumes of activation for a series of reactions, the mechanism of any one reaction can generally be assigned with reasonable

assurance independently of the others. This may be an advantage in a system in which experimental difficulties preclude the measuring of solvent exchange rates, and the like. Second, after allowance has been made for solvational effects, a positive ΔV^* has the same significance in one solvent as in another. Interpretation of the values of ΔH^* and ΔS^* obtained in different solvents is not as straightforward[30]. Indeed even in a single solvent, enthalpies and entropies are less readily understood than is the concept of volumes.

Since the dependence of reaction rates on pressure is relatively small, the measurement of activation volumes requires equipment capable of withstanding pressures of at least 200 MPa. For this reason comparatively few inorganic chemists have engaged in this type of research, and many questions have remained unanswered. Much is still to be learned about the temperature-dependence and the effect of changes in medium on ΔV^*. Also, relatively little work has been done on the volumes of activation for reactions of inert complex ions in nonaqueous solvents. The work to be described in subsequent chapters was thus undertaken not only for the purpose of learning about the mechanisms involved in the specific reactions chosen, but also in an effort to find answers to some of these questions about volume parameters in general.

CHAPTER 2

THE EFFECT OF PRESSURE ON THE RATE OF SOLVENT EXCHANGE OF DIMETHYLFORMAMIDEPENTAAMMINERHODIUM(III) ION IN DMF, AND REACTIONS OF THE ION WITH VARIOUS NUCLEOPHILES

1. Introduction

A large proportion of the kinetic studies which have been conducted on trivalent transition metal complex ions have involved cobalt(III) as the central metal. This is in part because a wide variety of cobalt(III) complexes can be prepared easily and inexpensively, and their reactions tend to be slow and thus readily studied by conventional kinetic methods. In addition to this, the mechanistic behavior of these complexes was thought to be typical of that of inert complexes. Thus when a large body of information seemed to indicate the operation of I_d and D mechanisms for most reactions of complexes of cobalt(III), it seemed probable that analogous complexes of other inert trivalent metals would also react via such mechanisms. Indeed, fast reaction techniques also led to the belief that the more labile divalent transition metals also favoured dissociative pathways.

In the late sixties and early seventies, reports began to appear which suggested that at least some complexes of trivalent transition metals such as titanium(III)[31], vanadium(III)[32], chromium(III)[18], molybdenum(III)[33], rhodium(III)[13,34] and iridium(III)[35] reacted by I_a mechanisms. Very recently it has been reported that I_a mechanisms may also occur in reactions of complexes of divalent manganese[36].

Since it now appears as though the behavior of cobalt(III) may be

exceptional rather than typical, more attention has begun to be focused upon the reactions of complexes of the other trivalent metal centres. Rhodium(III), being the second row congener of cobalt(III), and having a similar low spin d^6 configuration has been of particular interest.

The aquation and chloride anation reactions of the series of complexes $[Rh(Cl_n(OH_2)_{6-n}]^{3-n}$ (n = 0 - 6) in acidic aqueous solutions have been studied in some detail[6,9,37-43]. Palmer and Harris[6] have suggested that the results are consistent with the operation of D-type mechanisms throughout this series. With two or three exceptions, the occurrence of D-mechanisms in the series is not unexpected. The strict stereospecificity observed in this series, coupled with the markedly higher rate coefficients for reactions involving replacement of a ligand trans to a chloride ligand, is a clear indication of a strong trans-effect. Furthermore the complexes at one end of the series are anionic. The occurrence of D-mechanisms in the reactions of these anionic complexes is supported by the values of ΔV^* obtained by Kelm and his co-workers[43]. It is by no means clear, however, why the solvent exchange or anation reactions of $Rh(H_2O)_6{}^{3+}$ should proceed by D-pathways. Indeed the evidence cited in support of these mechanistic assignments is equivocal. The main points advanced were that the values of k_{an} were less than that of k_{ex} for anation of the $Rh(H_2O)_6{}^{3+}$ ion by Cl^- and Br^- [39,42], and that the acid-dependence of the observed anation rate constants was such as to preclude the possibility that the $Rh(H_2O)_6{}^{3+}$ ion and its conjugate base both reacted by means of interchange mechanisms. With regard to the first point, the k_{ex} value was measured in solutions of ionic strengths ranging from 5.8 M to 12 M[37]. Clearly under such extreme conditions the activity of water would be greatly reduced over that in the more dilute solutions

used in the anation studies. It is thus somewhat doubtful whether the k_{ex} value is comparable with the anation rate constants. In any event, it is quite possible to have anation rate constants which are less than k_{ex} in an I_a mechanism. The second point does not establish the operation of a D-mechanism in the reactions of $Rh(H_2O)_6{}^{3+}$ either. The acid-dependence criterion used does not distinguish between the possibility that $Rh(H_2O)_6{}^{3+}$ and $Rh(H_2O)_5OH^{2+}$ both react by a D-mechanism and the possibility that one reacts by an I-mechanism and one by a D-mechanism. Thus the mechanism by which chloroaquo rhodium(III) cationic complexes react in instances where the trans-effect is not important is left in doubt.

Complexes of the type $Rh(en)_2LX^{n+}$ have also been investigated[44-48], but mostly from the point of view of investigating the relative trans-activating abilities of various ligands[45-47]. Johnson et. al. have cited the lack of dependence of the rate coefficients for aquation of $Rh(en)_2Cl_2{}^{2+}$ and various other $RhA_4Cl_2{}^{n+}$ species (A = amine) on charge as evidence for the participation of the incoming water molecule in the transition state (I_a mechanism)[44]. Poë and co-worker[45], while not strongly favouring any particular mechanism, have criticised this argument on the basis that in changing the charge on the rhodium complex ion, the ligand trans to the leaving group has necessarily also been altered. Since kinetic trans-effects play a very important rôle in reactions of these complexes, any alterations of this sort may affect k_{aq} in such a way as to compensate for any changes which would otherwise have resulted from a variation in the charge of the complexes. Pavelich[48] has again used the acid-dependence of the observed rate coefficient to argue that the $Rh(en)_2(OH_2)_2{}^{3+}$ and $Rh(en)_2(OH_2)OH^{2+}$ ions do not both anate by way of interchange mechanisms. As in the case of the $Rh(H_2O)_6{}^{3+}/Rh(H_2O)_5OH^{2+}$ system, either

the diaquo or the conjugate base may anate by an interchange pathway, or both may react by D-routes.

The other well-studied series of rhodium(III) complexes is the pentaammine group. The reactions of these complexes have been investigated by many different groups over a period of some fifteen years. From the point of view of comparisons with analogous complexes of other metals, this is one of the most interesting series, since many cobalt(III) and chromium(III) pentaammines have been kinetically studied, as have those of ruthenium(III) and iridium(III) to a lesser degree. Unfortunately, agreement as to the mechanism of reaction of the rhodium pentaammines is by no means complete.

Monacelli and co-workers have studied reaction 14 for $X^{n-} = H_2O$ [49] and Cl^-, Br^-, SO_4^{2-} [13]. The solvent exchange reaction was assigned an I_a

$$Rh(NH_3)_5H_2O^{3+} + X^{n-} \longrightarrow Rh(NH_3)_5X^{(3-n)+} + H_2O \qquad 14$$

mechanism, in part because k_{ex} for the rhodium complex was greater than that for the analogous cobalt complex, which would not be expected if both metal centres reacted by the same I_d mechanism. In addition, ΔS^*_{ex} was more negative for the rhodium reaction than for the cobalt one. The anation reactions were also assigned I_a mechanisms, because the k_i values varied from one nucleophile to another and were all greater than or equal to k_{ex}. Monacelli's group also studied the spontaneous aquation of the sulphato-[50] and nitrato-[51]pentaammines. Both processes were rather ambiguously described as being essentially dissociative with partial associative character. For the sulphato complex at least, the mechanism must be I_a, since the anation process apparently is. The Principle of Microscopic Reversibility requires that the forward and reverse reactions must both go through the same transition state, and thus via the same

mechanism.

Chan[52] studied the aquation of the halopentaamminerhodium(III) complexes ($X^- = Cl^-, Br^-, I^-$). By analogy with S_N2 reactions of organic aromatic compounds, he rationalised the relative reactivities of the three complexes in terms of a rate-determining step in which bond-making is predominant.

Poë et. al.[47] have pointed out some interpretational difficulties encountered when comparing the relative magnitudes of k_i and k_{ex}. However, after estimating the possible effects resulting from ion-pairing by the inert counter-ion ClO_4^-, and from changes in the composition of the medium as the reaction proceeds, the authors concluded that k_i would still be greater than k_{ex}, and at least some associative character would exist in the mechanism of anation. These problems were also considered by Pavelich, Maxey and Pfaff[16]. Rather than attempting to estimate the magnitude of these effects, the kinetics of chloride anation of the $Rh(NH_3)_5OH_2^{3+}$ ion were studied under conditions of very low ionic strength to minimize them. These authors assert that the "pure" interchange rate coefficient, corrected for perchlorate ion-pairing, is less than k_{ex} for $X = Cl^-$. Van Eldik[53] has also found that k_i is less than k_{ex} for anation of $Rh(NH_3)_5OH_2^{3+}$ by various oxalate species, and has used this observation as evidence for the occurrence of an I_d mechanism. While a k_i which is smaller than k_{ex} is consistent with the operation of an I_d mechanism, it is not inconsistent with the occurrence of an I_a mechanism. Thus a decision cannot be made on this basis alone.

Swaddle and Stranks[54] reported the ΔV^* for aquo-exchange by $Rh(NH_3)_5OH_2^{3+}$ to be -4.1 $cm^3\ mol^{-1}$, and indicated that this was clear evidence for the operation of an I_a mechanism. Recently Kelm and his

colleagues[55] have cited a value of +3.0 cm^3 mol^{-1} for the ΔV^* of the chloride anation of $Rh(NH_3)_5OH_2^{3+}$, and have suggested the operation of an I_d mechanism in consequence. In so doing, they have assumed that the volume changes on formation of the ion-pair and arising from the solvational contribution to the interchange step are both zero. It would seem to be a rather extreme assumption to suggest that no change in volume would result from solvational changes accompanying ion-pair formation and interchange, even in 2.0 M electrolyte. Even small contributions from these two sources could be sufficient to overwhelm a negative bond-making contribution, and lead to the observed slightly positive ΔV^*. In this instance the ΔV^* value obtained is too small to allow a reliable assignment of mechanism to be made in a system in which solvational changes must be important at some stage.

The effect on k_{aq} of changing R in $Rh(NRH_2)_5Cl^{2+}$ from R = H to R = CH_3 is that the rate coefficient is slightly decreased[56]. This has been interpreted in terms of the operation of an I_a mechanism in which the degree of steric crowding resulting from N-methylation of the amine is greater in the transition state than in the starting complex. In the analogous cobalt(III) complexes, an acceleration of aquation occurs upon N-methylation of the amine, which is to be expected for a system reacting via an I_d mechanism.

In light of the uncertainty which still exists as to whether any one mechanism predominates in the reactions at rhodium(III) centres, the work to be described below was undertaken in the hope that studies in a different solvent might help to resolve some of the conflicts.

The effects of changes in temperature and pressure on the rate of the solvent exchange reaction given in equation 15 were investigated, in DMF as solvent.

$$Rh(NH_3)_5DMF\text{-}d_7^{3+} + DMF \xrightarrow{k_{ex}} Rh(NH_3)_5DMF^{3+} + DMF\text{-}d_7 \qquad 15$$

Attempts were also made to study the anation reaction given in 16 using $X^- = Cl^-$, Br^- and NCS^-.

$$Rh(NH_3)_5DMF^{3+} + X^- \underset{}{\overset{K}{\rightleftharpoons}} \{Rh(NH_3)_5DMF^{3+}, X^-\}$$

$$\xrightarrow{k_i} Rh(NH_3)_5X^{2+} + DMF \qquad 16$$

The use of dipolar aprotic solvents such as DMF in kinetic studies has the advantage of eliminating conjugate base pathways involving solvent. Furthermore, k_i can often be measured directly, since in solvents of low dielectric constant relative to water (DMF 36.7; H_2O 78.3 at 25°C) complete ion-pairing of the reactants is easily attainable even at moderate concentrations. Unfortunately the low dielectric constant frequently limits the range of conditions under which the reactions may be studied, because the solubility of most electrolytes is substantially reduced in such a medium.

2. Experimental

2.1 Materials

Perdeuterated DMF (99.5% D, Stohler Isotopes) was diluted to approximately 7% using purified DMF of natural isotopic composition. 70-72% perchloric acid (Baker Analyzed), trifluoromethanesulphonic acid (Eastman), *para*-toluenesulphonic acid monohydrate (Fisher), and tetraethylammonium chloride (Eastman) were used without further purification. Potassium thiocyanate (Fisher) was recrystallized from hot acetone by the addition of ether. Tetraethylammonium bromide (Eastman) was recrystallized from DMF in the same manner.

Purification of DMF

The DMF (usually Baker Analyzed) was stored over 4A molecular sieves (Fisher) which had been dried at 200°C before use. Not more than twenty-four hours before a run, the DMF was distilled slowly under reduced pressure (water aspirator) through a 30 cm vacuum-jacketed column packed about half full with glass helices. The initial and final 15% of the distillate was discarded. In later runs, a dry ice/acetone trap was installed between the still and the aspirator, and a thin stream of dry nitrogen (Linde) was passed through the system throughout the distillation.

The index of refraction of this purified solvent, measured at 26°C using the D-line of sodium, was 1.4295. The value corrected to 20°C was 1.4305, in exact agreement with the literature value[57].

N,N-dimethylformamidepentaamminerhodium(III) perchlorate

$[Rh(NH_3)_5OH_2](ClO_4)_3$ was prepared from $[Rh(NH_3)_5Cl]Cl_2$ by refluxing an aqueous suspension of the latter complex with $AgClO_4$ [54]. The aquopentaamminerhodium complex was then dissolved in the minimum of water, to which had been added one drop of concentrated hydrochloric acid. The solution was filtered to remove any silver chloride present, then the complex was reprecipitated by the addition of 72% perchloric acid. The silver-free aquopentaammine complex (2 g) was dissolved in 6 mL of DMF (7% DMF-d_7 if labelled product was desired) and warmed on a steam-bath for three hours. The solution was cooled in ice, then 6 mL each of water and 72% perchloric acid were added to precipitate the product. The pale yellow material was recrystallised from DMF by the addition of 36% aqueous perchloric acid, washed with a 20% solution of acetone in ether, and dried in a vacuum desiccator over P_2O_5. The yield was 1.5 - 1.6 g.

The 60 MHz proton magnetic resonance spectrum of the product in DMSO-d_6 showed signals of equal intensity at 6.48 τ and 6.67 τ due to the two methyl groups of DMF, and a third resonance at 2.07 τ attributable to the aldehydic proton. The room temperature ultraviolet spectrum exhibited an absorption maximum at 323 nm (ε = 216 L mol^{-1} cm^{-1}).

Analysis (Alfred Bernhardt Microanalytical Laboratory)

Calculated for $[Rh(NH_3)_5DMF](ClO_4)_3$:

C 6.44, H 3.96, Cl 19.01;

Found: C 6.60, H 3.94, Cl 18.89.

N,N-dimethylformamidepentaamminerhodium(III)tetrafluoroborate

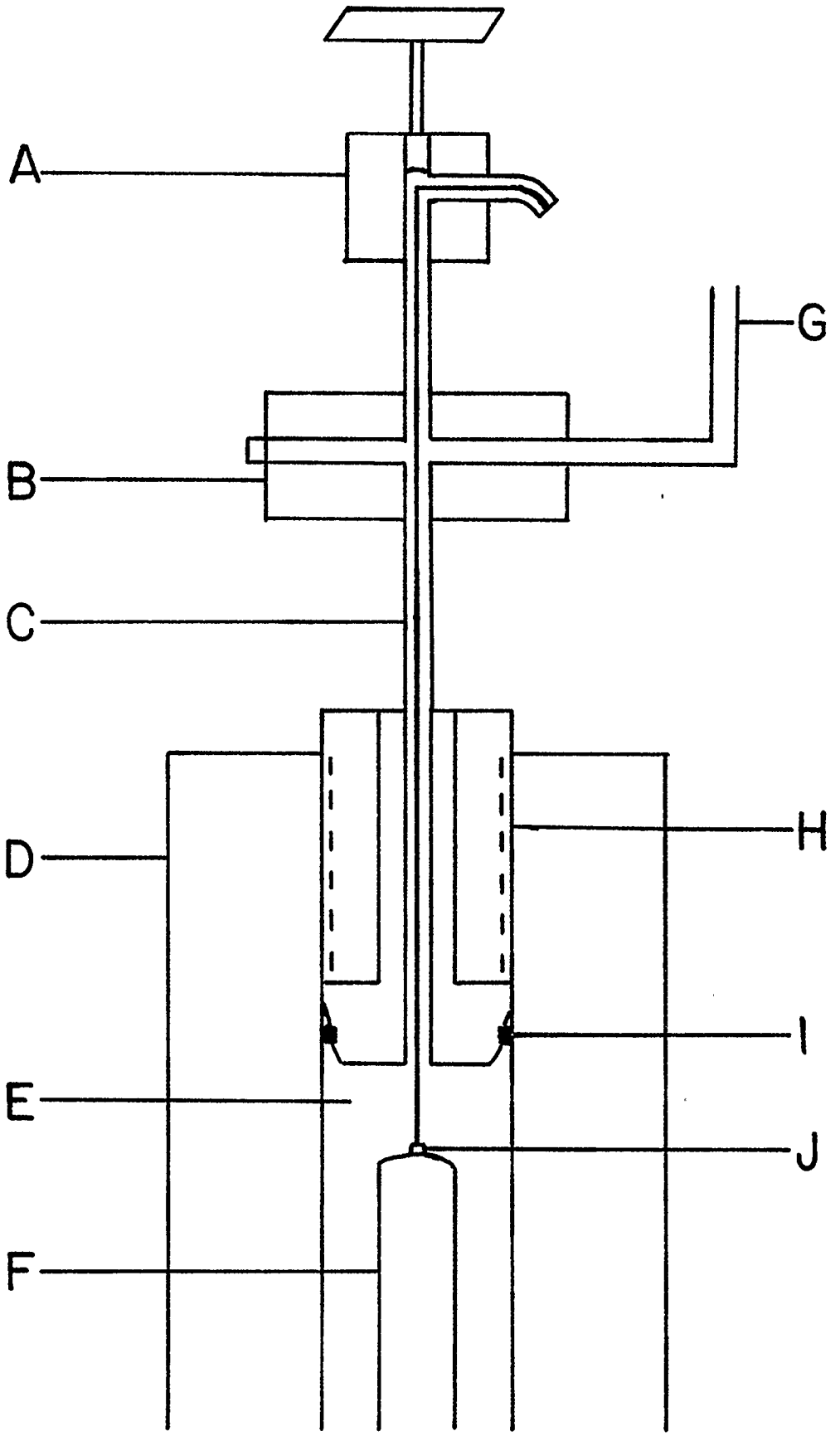
This complex was prepared in the same way as the perchlorate salt, except that 48% aqueous tetrafluoroboric acid (Ventron) was used in place of the water and perchloric acid in the precipitation and recrystallization steps. Also, the product was washed with ethanol rather than acetone, since it was significantly soluble in the latter.

2.2 High Pressure Apparatus

Kinetic runs were conducted under pressures ranging from 10 to 400 MPa in the assembly shown schematically in figure 2. The reaction solution was contained in an ordinary glass syringe (Becton-Dickinson) attached to the pressure head (Autoclave Engineers, Inc.) by means of a tantalum capillary. Tantalum was chosen over stainless steel because of its unreactivity in the presence of warm, acidic solutions. The pressure in the vessel was automatically maintained by means of an air-driven hydraulic pump (American Instrument Co.) controlled by a photoelectric device mounted on the face of the pressure gauge. Thus samples could be withdrawn at various times, without a significant drop in pressure

Figure 2

High Pressure Assembly
A. Sampling Valve, B. Junction Box, C. Tantalum Capillary, D. Pressure Vessel, E. Hydraulic Oil, F. Glass Syringe, G. Connection to Pump and Gauge, H. Sealing Nut, I. Buna Rubber O-Ring, J. Luer Lock.


A
G
B
C
D
H
I
E
J
F

occurring in the process. The reservoir of oil in the junction box ensured that the oil replacing the solution run out was at the same temperature as the reaction solution. The pressure vessel and junction box were thermostatted in an oil bath whose temperature was controlled to within ±0.01°C by a Melabs CTC-1A proportional temperature controller. The pressure gauge, of the Heise Bourdon tube type, had been calibrated using a dead-weight gauge, and shown thus to be accurate to within ±1%.

2.3 Kinetics

2.3.1 Solvent Exchange

All atmospheric pressure experiments were conducted in stoppered, darkened Pyrex vessels. To initiate a run, a weighed amount of 7% DMF-d_7 labelled $[Rh(NH_3)_5DMF]^{3+}$ as the perchlorate or tetrafluoroborate salt was added to freshly distilled DMF containing a known amount of acid (usually trifluoromethanesulphonic), which had prior to this been brought to the desired reaction temperature. At appropriate times, samples containing about 4×10^{-4} moles $[Rh(NH_3)_5DMF]^{3+}$ were withdrawn and delivered into ice-cold DMF containing 5×10^{-3} moles tetraethylammonium chloride. The $[Rh(NH_3)_5DMF]Cl_3$ obtained was filtered, washed thoroughly with acetone, and dried at 70°C under house vacuum. The samples were decomposed on the vacuum line by heating them carefully to 175±5°C. The DMF evolved was collected in tubes chilled in liquid nitrogen, and isotopically analyzed by passing it into a Varian MAT CH 5 mass spectrometer.

The high pressure runs were conducted in exactly the same way, except that the reaction solution was contained in the pressure assembly described earlier, and that para-toluenesulphonic acid monohydrate replaced the trifluoromethanesulphonic acid.

2.3.2 Reactions of $[Rh(NH_3)_5DMF]^{3+}$ with Anions

In general, a solution of $[Rh(NH_3)_5DMF](ClO_4)_3$ and para-toluenesulphonic acid monohydrate in DMF was brought to the desired reaction temperature, as was a solution of the nucleophile in DMF. To begin the runs, aliquots of the two solutions were mixed together and transferred to a quartz cell thermostatted in an aluminium block. The block temperature was controlled to ±0.1°C by means of a Melabs CTC-1A proportional temperature controller. The reaction was followed *in situ* by means of a Cary Model 17Hc spectrophotometer.

Some runs in which the nucleophile was bromide were followed by removing samples from darkened, stoppered Pyrex vessels thermostatted to ±0.01°C in a Sargent thermonitor bath filled with paraffin oil, and running them singly in the spectrophotometer.

3. Results

3.1 Solvent Exchange

The fraction x of d_7-labelled solvent in a sample of DMF is given, to a close approximation, by equation 17. Direct measurement of m/e 80

$$x = \frac{\text{intensity m/e 80}}{\text{intensity m/e 73} + \text{intensity m/e 80}} \qquad 17$$

relative to m/e 73 necessitates the switching of ranges on the mass spectrometer which increases the error in the measurement. To circumvent this, m/e 74 is measured instead of m/e 73. The intensities of these two peaks are related in equation 18.

$$(\text{intensity m/e 74}) = 0.0387\ (\text{intensity m/e 73}) \qquad 18$$

On combining these two relationships, equation 19 is obtained.

$$x = \frac{1}{1 + 25.84\ (1/R)} \qquad 19$$

R is the ratio of the intensity of m/e 80 relative to that of m/e 74, and is the experimentally determined quantity.

The solvent exchange data were fitted to an equation of the form given in equation 20 using a standard linear least squares program.

$$\ln\ (x_t - x_\infty) = k_{ex}t + \ln\ (x_0 - x_\infty) \qquad 20$$

In this equation, x_0, x_t, and x_∞ refer to the fractions of DMF-d_7 present at zero time, time t, and infinite time, respectively. The reaction followed first-order kinetics over at least the first two half-lives. A typical plot of $\ln\ (x_t - x_\infty)$ versus time is shown in figure 3, and the pseudo-first-order rate coefficients k_{ex} for the solvent-exchange process are given in table 2.

The Eyring equation was used to determine the enthalpy and entropy of activation which are 99.1±2.0 kJ mol^{-1} and -19.8±6.0 J K^{-1} mol^{-1}, respectively, when $[Rh(NH_3)_5DMF^{3+}] = [CF_3SO_3H] = 0.245$ M. A plot of $\ln k_{ex}$ against pressure is shown in figure 4. The results are not precise enough to show whether any curvature is present, mainly because the effect of pressure on k_{ex} is particularly small for this reaction. Using a linear least squares treatment a ΔV^* of -1.4±0.2 cm^3 mol^{-1} for $[Rh(NH_3)_5DMF^{3+}]$ = [p-toluenesulphonic acid] = 0.051 M and T = 44.8°C is obtained. The results from the high pressure experiments extrapolated to 0.1 MPa give $k_{ex} = 3.68 \times 10^{-5}\ s^{-1}$ in very good agreement with the value $3.72 \times 10^{-5}\ s^{-1}$ obtained experimentally in ordinary glassware.

Figure 3

Typical plot of ln $(x_t - x_\infty)$ vs. Time for solvent exchange of $[Rh(NH_3)_5DMF]^{3+}$ in DMF. T = 44.82°C, P = 399.5 MPa.

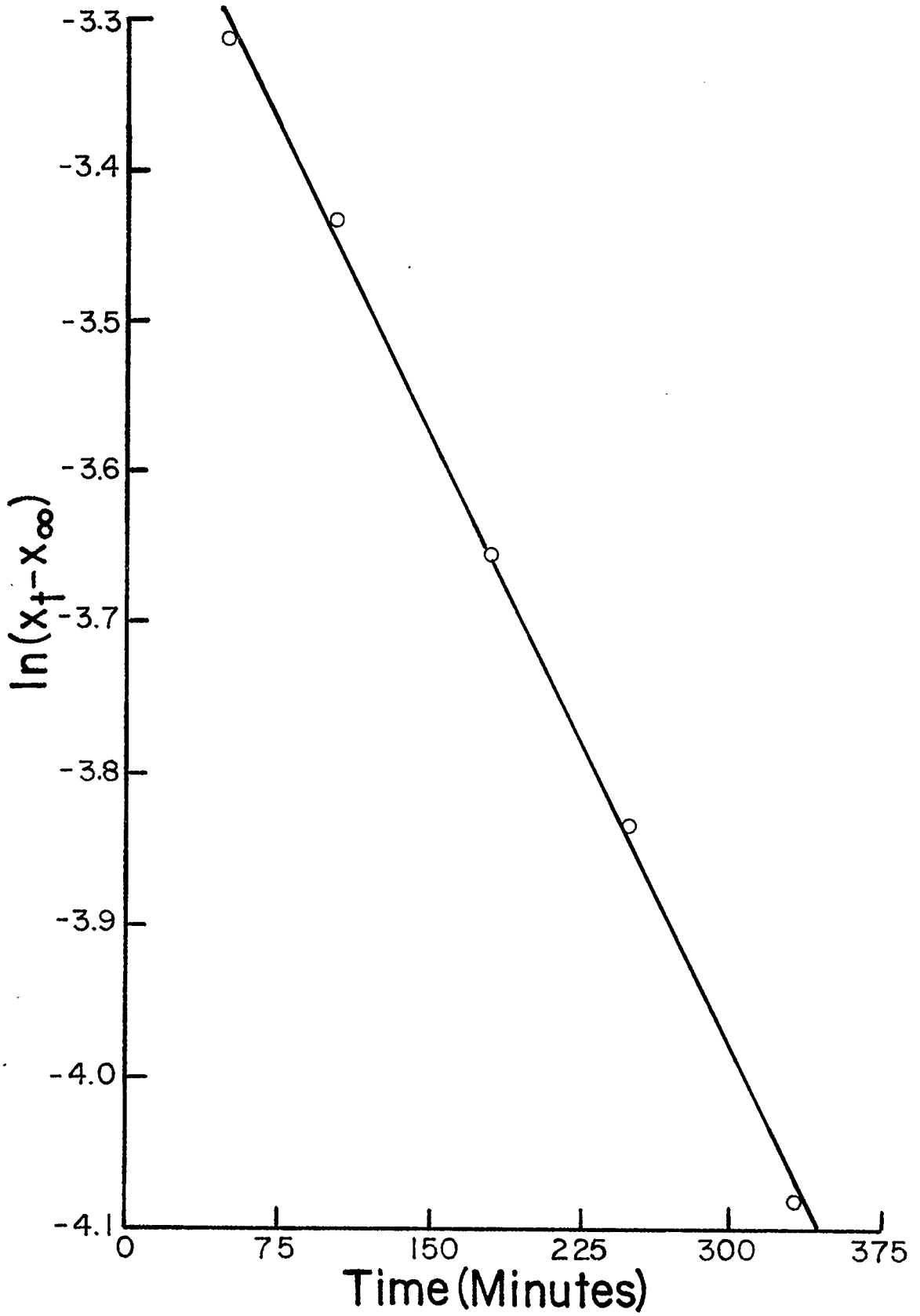

-3.3
-3.4
-3.5
-3.6
-3.7
-3.8
-3.9
-4.0
-4.1
ln(X_t-X_∞)
0
75
150
225
300
375
Time (Minutes)

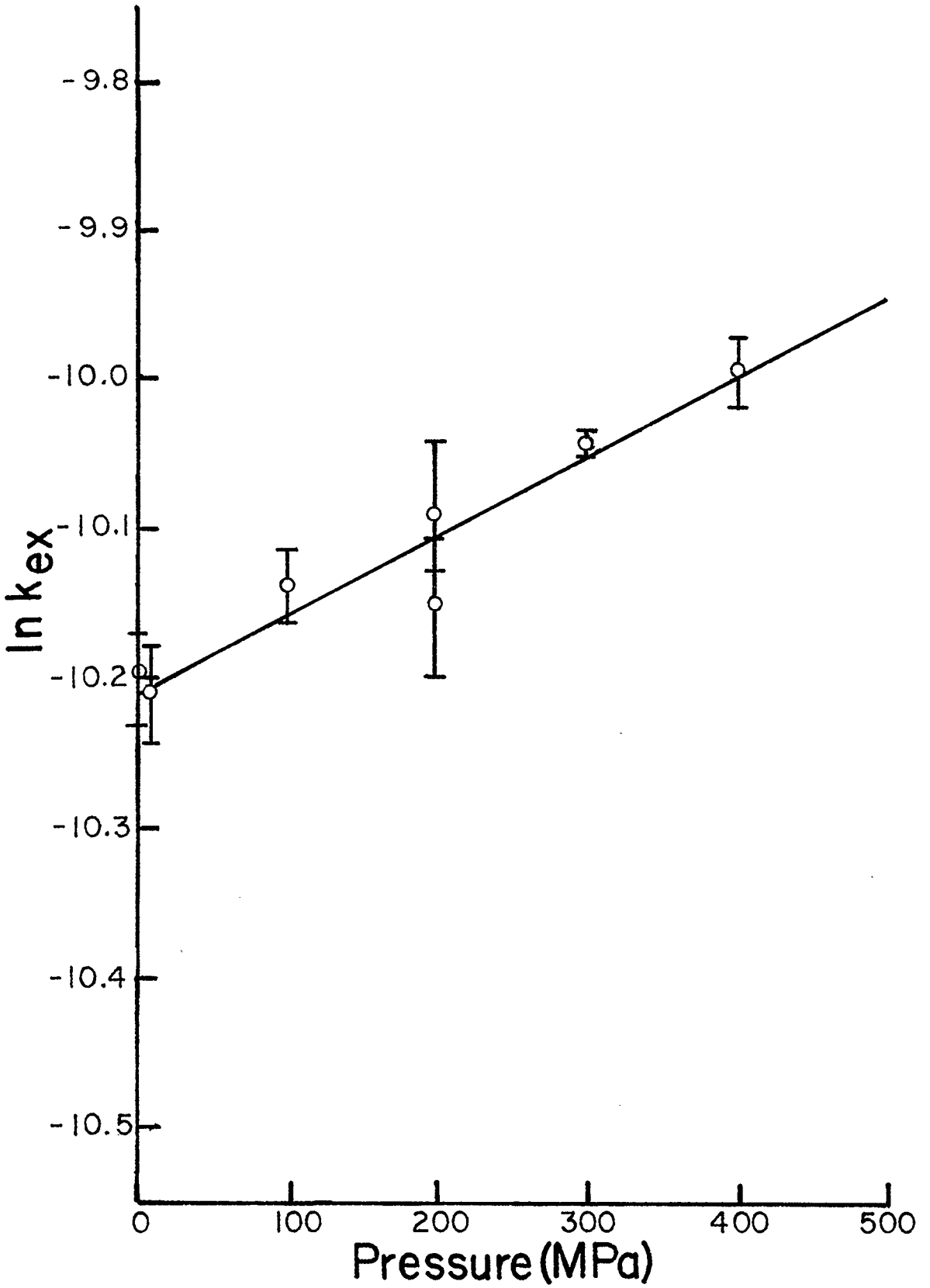
Table 2. Pseudo-First-Order Rate Coefficients for DMF Exchange Between $[Rh(NH_3)_5DMF]^{3+}$ and DMF Solvent

Temperature °C	Concentration $Rh(NH_3)_5DMF^{3+}$ (mol L^{-1})[a]	Concentration Acid (mol L^{-1})	Pressure (MPa)	$10^5\ k_{ex}(s^{-1})$
25.00	0.245	0.245[b]	0.1	0.244±0.009
45.00	0.063	0		3.52±0.012
	0.245	0		3.30±0.011
		0.245[c]		3.13±0.010
55.00	0.031	0		13.2±0.2
	0.245			11.3±0.3
	0.245[d]			11.3±0.3
		0.245[b]		10.6±0.3
44.82	0.051	0.051[c]		3.72±0.12
			9.2	3.67±0.12
			100.5	3.95±0.10
			201.2	3.90±0.18
			202.0	4.14±0.20
			303.4	4.34±0.05
			399.5	4.56±0.10

a Perchlorate Salt unless otherwise stated
b Trifluoromethanesulphonic Acid
c Para-toluenesulphonic Acid Monohydrate
d Tetrafluoroborate Salt

Figure 4

Pressure-Dependence of k_{ex} for $[Rh(NH_3)_5DMF]^{3+}$ in DMF.
[Complex] $\cong$ [Acid] = 0.051 M,
T = 44.82°C.


-9.8
-9.9
-10.0
-10.1
-10.2
-10.3
-10.4
-10.5
ln kex
0
100
200
300
400
500
Pressure (MPa)

3.2 Reactions with Anions

All attempts at measuring the rate coefficients k_{an} for anation of $Rh(NH_3)_5DMF^{3+}$ by various nucleophiles ended in failure. For $X^- = Cl^-$, immediate precipitation of $[Rh(NH_3)_5DMF]Cl_3$ occurred upon mixing of the two reactant solutions, even when the concentration of complex was as low as 2×10^{-4} M. Since the tails of the fully-allowed DMF absorptions occurring in the ultraviolet region of the spectrum obscure the charge transfer bands of the complex, it was not possible to monitor the reaction at low wavelengths, and thus the concentrations could not be lowered any further.

When $X^- = Br^-$, *in situ* monitoring of the anation reaction was hampered by the occurrence of a seemingly photochemically induced oscillating reaction. A small portion of the spectrophotometer trace, showing the rather remarkable fine structure, is given in figure 5. When the wavelength was changed from 324 nm to 370 nm, oscillations with the same period, but of lower intensity, were observed. The intensity, however, seemed to increase with time. It should be noted that the absorbance of the solution increased with time, although a decrease would have been expected for the anation process. This may have been an indication that the early stages of precipitate formation had begun, even though no crystals were visible to the eye. Noyes[58] has thus suggested that the observed cyclic behavior may have been due to a periodic precipitation phenomenon such as the formation of Liesegang rings, rather than to an oscillating chemical reacton. Flicker and Ross[59] have pointed out that a periodic distribution of substance exists before the appearance of visually perceptible rings, and that such a precipitation phenomenon may occur in an initially homogeneous solution. While the phenomenon observed here is probably not the formation of true Liesegang rings, some

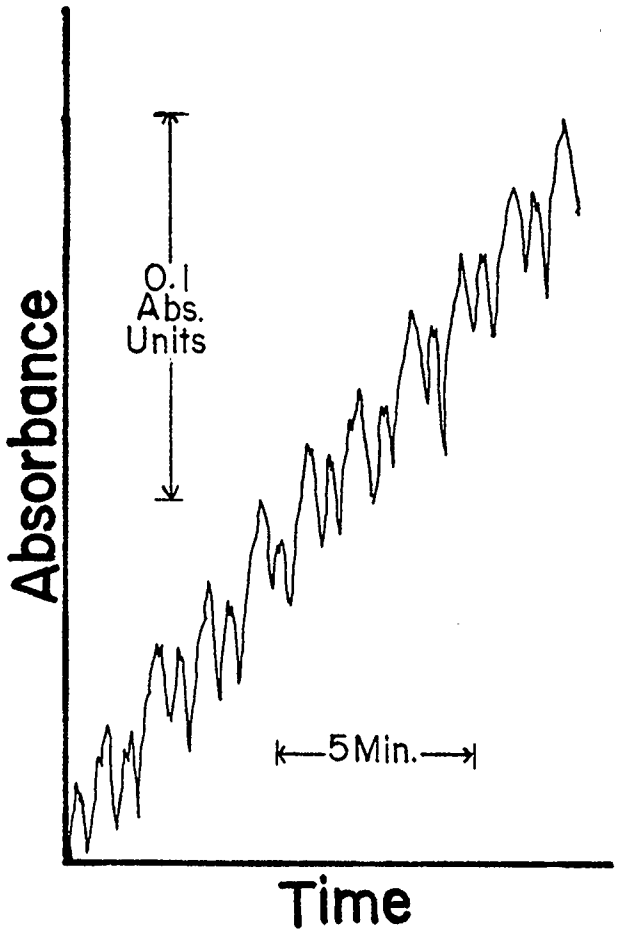


Figure 5. Oscillations observed at 324 nm during *in situ* monitoring of $[Rh(NH_3)_5DMF](ClO_4)_3$ + Et_4NBr in DMF.

sort of periodic precipitation seems likely.

The attempts at measuring the bromide anation rate by withdrawing samples from darkened Pyrex vessels equilibrated in an oil bath and measuring their absorbances individually, failed due to precipitation of the bromide salt of the starting or product complex (or both).

When the nucleophile used was NCS^-, two consecutive reactions were

found to be occurring. This was particularly evident at 15°C where the faster step was clearly distinguishable from the slower one. Because the reaction rates for the two steps were of the same order of magnitude, and precipitation of the product prevented the reactions from being followed to completion, the rate data for the two steps could not be resolved. It was clear, however, that when $[Rh(NH_3)_5DMF^{3+}] = 1.28 \times 10^{-3}$ M and $[NCS^-] = 1.30 \times 10^{-1}$ M, one reaction was somewhat slower ($k \sim 2 \times 10^{-5}$ s^{-1}) than solvent exchange ($k = 3.68 \times 10^{-5}$ s^{-1}) and the other slightly faster ($k \sim 4.5 \times 10^{-5}$ s^{-1}). Presumably the two reactions involved were formation of the S-bonded thiocyanato complex followed by a slower isomerisation to the thiocyanato-N-pentaamminerhodium(III) ion. Both linkage isomers are known, and the N-bonded product has been shown to be the thermodynamically more favourable product, at least in aqueous solutions[60].

No attempt was made to use azide as the attacking nucleophile, since this anion would probably have abstracted a proton from the weakly acidic ammine ligands and thereby introduced mechanistic complications such as those observed in the aquation of the azidopentaaquochromium(III) complex[61].

4. Discussion

4.1 Solvent Exchange

4.1.1 Effect of Changing the Composition of the Reaction Solution

As the data in table 2 show, k_{ex} is not much altered when the concentration of acid is changed from 0 to 0.245 mol L^{-1}. This is in marked contrast to the behavior of the analogous cobalt(III) system[15] in which k_{ex} is decreased by a factor of about fifty when the acid concentration is raised in a comparable fashion. Furthermore, in the cobalt system, reduction of the metal(III) centre to a metal(II) centre occurs

at low acidities. The solventopentaamminecobalt(III) complex exhibited similar behavior in DMSO as solvent[14]. Both the higher k_{ex} at low acidities and the reduction were attributed to conjugate base pathways involving loss of a proton from one of the ammine ligands giving a labile amidotetraammine intermediate. Whereas rhodium complexes containing ligands with ionisable protons do undergo D_{cb} reactions in aqueous solutions, in general rhodium complexes seem to do so much less readily than their cobalt analogues. This may be due to the inability of rhodium to stabilise the conjugate base intermediate by means of π-bonding. Furthermore, rhodium(III) is much less easily reduced than is cobalt(III), presumably because the ligand field splitting parameter for the former metal is about 50% larger than that of the latter[62], making the empty e_g orbitals of rhodium(III) less accessible to extra electron density. The slight decrease in k_{ex} (∿ 5%) which is observed in the $Rh(NH_3)_5DMF^{3+}$/DMF system upon addition of acid is likely due to an increase in ionic strength. Such a decrease may be due to increased ion-pair formation between the complex cation and the counter-ion of the acid. If the anion occupies a position in the second coordination sphere which is adjacent to the coordinated DMF ligand, interchange of this DMF with a DMF molecule in the second coordination may be blocked, and k_{ex} reduced. Alternatively (or, in addition) the activity of the solvent DMF may be reduced somewhat at higher ionic strengths.

Table 2 also shows a slight decrease in k_{ex} with increasing complex concentration. This is likely also due to the ionic strength effect mentioned above.

Substitution of the tetrafluoroborate salt of the complex cation for the perchlorate salt has no effect at all on k_{ex}. Thus, whereas univalent anions in general exert a very small medium effect on k_{ex},

ClO_4^- in particular causes no specific effect.

The use of p-toluenesulphonic acid monohydrate in the non-aqueous solutions does not appear to affect k_{ex}, in spite of the fact that in so doing one introduces a mole of water for every mole of complex. Such insensitivity to moisture is by no means a general feature of kinetics in DMF as will be seen in Chapter 3.

4.1.2 Temperature-Dependence of k_{ex}

The ΔH_{ex}^* and ΔS_{ex}^* parameters derived for reaction 15 from the temperature-dependence of k_{ex} are collected in table 3, together with the analogous parameters for solvent exchange in several other pentaammine-metal(III) systems. Comparing ΔH_{ex}^* and ΔS_{ex}^* values for different metal centres in the same solvent, it can be seen that slightly smaller ΔH_{ex}^*'s and substantially more negative ΔS_{ex}^* values are obtained for rhodium than for cobalt in both water and DMF. As was argued for the aquo-exchange results[49,54], the lower values for rhodium in DMF suggest that bond-making (I_a mechanism) is of importance in the transition state for solvent exchange at the pentaamminerhodium centre. If the rhodium complex reacted by the same I_d mechanism as does cobalt(III), a higher ΔH_{ex}^* would be expected for the rhodium reaction than for the cobalt, since dissociation of a ligand would result in a larger loss of ligand field stabilization energy (LFSE) from the former metal than from the latter. In an I_a mechanism, LFSE is no longer the major contributor to ΔH_{ex}^*, since the increased covalency of the metal centre compensates to a large extent for the loss of LFSE[4a]. The more negative ΔS_{ex}^* for rhodium relative to cobalt is indicative of the higher degree of ordering which occurs on going to the transition state in the rhodium system.

Table 3. Activation Parameters for
$M(NH_3)_5{}^*S^{3+} + S \longrightarrow M(NH_3)_5S^{3+} + {}^*S$

Central Metal	Solvent	ΔH_{ex}^* kJ mol^{-1}	ΔS_{ex}^* J deg^{-1} mol^{-1}	ΔV_{ex}^* cm^3 mol^{-1}
Rh(III)	DMF[a]	99.1±2.0	-19.8±6.0	-1.4±0.2
	H_2O[b]	103.0±2.0	+3.4±4.6	-4.1±0.4
Ir(III)	H_2O[c]	117.6±1.3	+11.3±4.2	-3.2±0.1
Cr(III)	H_2O[b]	97.1±2.1	0±6.7	-5.8±0.2
Co(III)	DMF[d]	113.4±1.2	+21.6±3.8	+3.2±0.1
	DMSO[e]	123±2	+61±6	+10.0±1.2
	H_2O[f]	111.4±1.3	+28.0±4.2	+1.2±0.2

a This Work
b Reference 54
c Reference 63
d Reference 15
e Reference 14
f Reference 64

4.1.3 Pressure-Dependence of k_{ex}

The rate of solvent exchange in DMF showed a slight but unmistakable acceleration with increasing pressure, characterised by a ΔV_{ex}^* of $-1.4\ cm^3\ mol^{-1}$. The usual practice, as described in chapter 1, has been to assign the mechanism of solvent exchange reactions on the basis of the sign of ΔV^*. Thus DMF exchange at $Rh(NH_3)_5DMF^{3+}$ would be assigned an I_a mechanism. In a very recent paper by Langford[65], this approach has been questioned. He suggests that the change in volume arising from movement of the non-reacting ligands in going to the transition state may make a major contribution to the observed ΔV^*. He implies, in fact, that for certain metal centres this component is so important that it can lead to a ΔV^* of opposite sign to that which would be expected on the basis of the intimate mechanism of the reaction. For an I_d mechanism, loss of the outgoing ligand causes contraction of the bonds to the five remaining ligands, thereby causing an increase in electron density at the metal centre. Such a contraction is thought by Langford to be least significant in ions having a spin-paired d^6 or a d^8 configuration, since in these cases the increased electron density would of necessity be accepted into high energy antibonding orbitals. Furthermore, the contraction is least significant for small non-polarisable metal centres such as Co(III). Thus Langford suggests that this contraction will make a larger contribution to the ΔV_{ex}^*'s of Cr(III) and Rh(III) than of Co(III). He does acknowledge that if there is some degree of associative character in the reactions of Cr(III) and Rh(III), the volume change associated with the entry of the attacking ligand into the first-coordination sphere may make a small contribution. He implies, however, that in the absence of other evidence in support of an associative contribution to the activation process, the obtaining of a negative ΔV_{ex}^*

is not diagnostic of an I_a process, but may only indicate a sizeable contribution of the metal-to-inert-ligand bonds.

The idea that a change in coordination number on going to the transition state might cause a change in the bond lengths to the non-reacting ligands is not new. Gutmann[27] has discussed what he calls the "pressure-distance paradox". Pressure, which may be formally regarded as being an electron donor, causes an increase in the density of a material. Nevertheless, while the overall density increases, some of the bond lengths become longer. In the crystal lattices with which Gutmann was dealing, intramolecular distances increased with increasing pressure, while intermolecular distances decreased. The net increase in density indicated that the intermolecular decrease was of greater importance than the intramolecular increases. Thus, while the theories of Gutmann and Langford both suggest that the non-reacting ligands should make a contribution to ΔV^*, Langford has suggested a more dominant rôle than would be expected on the basis of Gutmann's arguments.

Langford's suggestion that the contraction of the metal-ligand bonds should be of greater importance for metals lying to the left of Co(III) in the periodic table (e.g. Cr(III)) and for metals in the second and third transition series (e.g. Rh(III)) does not seem reasonable. The ability of Cr(III) and Rh(III) to accept the extra electron density resulting from a contraction of the metal-ligand bonds is in fact less than that of Co(III) if ease of reduction is any indication. In any event, if Cr(III) and Rh(III) react via I_a mechanisms, the bonds to the "inert" ligands may become longer not shorter on going to the transition state, because of the increase in coordination number of the central metal ion. In that case ΔV_{ex}^* would be less negative than expected on the basis of the intimate mechanism, not more negative as suggested by Langford. As

an example, Langford's hypothesis predicts that in going from rhodium(III) to iridium(III), the "contractibility" would increase, and hence a more negative value of ΔV_{ex}^* would be expected for $Ir(NH_3)_5OH_2^{3+}$ than for $Rh(NH_3)_5OH_2^{3+}$. The observed ΔV_{ex}^*'s are -4.1±0.4 cm^3 mol^{-1} (Rh) and -3.2±0.1 cm^3 mol^{-1} (Ir), which is contrary to what was predicted.

Whereas consideration of the volume contribution made by the non-reacting ligands is necessary if an interpretation of the magnitude of ΔV_{ex}^* is to be made, there seems little reason at this stage to doubt that the sign of ΔV_{ex}^* is diagnostic of mechanism. Therefore, the values in the last column of table 3 suggest that $Rh(NH_3)_5DMF^{3+}$ like $Rh(NH_3)_5OH_2^{3+}$, $Ir(NH_3)_5OH_2^{3+}$, and $Cr(NH_3)_5OH_2^{3+}$, undergoes solvent exchange by an I_a process, while the solventocobalt(III) complexes react via I_d pathways.

The absolute magnitude of ΔV_{ex}^* for $Rh(NH_3)_5DMF^{3+}$ is very small. In the case of $Co(NH_3)_5H_2O^{3+}$, the magnitude of ΔV^* was rationalised in terms of the difference in molar volume between water in the first coordination sphere and that in the second, which was calculated to be about 1 cm^3 … mol^{-1} [66] (cf. ΔV_{ex}^* +1.2 cm^3 mol^{-1}). For an I_a process, such as has been suggested for the $Rh(NH_3)_5DMF^{3+}$ solvent exchange, the volume change to be expected is much more difficult to predict, since the entry of the attacking nucleophile into the first coordination sphere is synchronous with the outward movement of the leaving group. The lengthening of the bond to the leaving group would tend to make ΔV_{ex}^* less negative than would be expected, as would the lengthening of bonds to the non-reacting ligands. The planarity of the formyl group in DMF may also lead to a lower compressibility for this solvent than might otherwise be the case. Even in the I_d Co(III) solvent exchange reactions, ΔV_{ex}^* in DMF is numer-

ically small compared to that for DMSO which has a similar molar volume (71.0 $cm^3\ mol^{-1}$ vs. 77.0 for DMF at 20°C, 0.1 MPa).

4.1.4 Reactions of $Rh(NH_3)_5DMF^{3+}$ with Nucleophiles

Due primarily to precipitation phenomena, few conclusions may be drawn about the mechanism of anation of $Rh(NH_3)_5DMF^{3+}$ in DMF. Anation by thiocyanate occurs at a rate which is slightly (∿ 20%) faster than that of solvent exchange. There are insufficient data to indicate whether or not a limiting rate (complete ion-pairing) had been reached, and thus k_i might actually be greater than the observed rate coefficient. In any case, $k_i > k_{ex}$. As discussed in chapter 1, however, the relative magnitudes of k_i and k_{ex} are not diagnostic of mechanism in non-aqueous solvents such as DMF. The more useful parameter ΔH_i^* could not be determined in this case.

The ultimate product of the thiocyanate anation of $Rh(NH_3)_5DMF^{3+}$ indicates that, as is the case with the analogous aquopentaammine-rhodium(III) complex in water[60b], the dimethylformamide complex in DMF exhibits class (a)[67] or "hard"[68] behavior. That is, $Rh(NH_3)_5DMF^{3+}$ shows a greater tendency to form complexes with small, non-polarisable (hard) ligands than with large, polarisable (soft) ligands. This preference of a hard acid for hard bases is usually interpreted as an indication of the formation of ionic or polar bonds, rather than covalent bonds. Rhodium(III) tends to be borderline in the (a)/(b) classification scheme, with the hardness or softness of its ligands being the determining factor in any given instance.

5. Conclusions

The values of the exchange activation parameters for $Rh(NH_3)_5DMF^{3+}$ in DMF support the assignment of an I_a mechanism for the pentaamminerhodium(III) series of complexes. Corroborative evidence in the form of a comparison of ΔH_i^* with ΔH_{ex}^* could not be obtained because precipitation phenomena and isomerisation prevented the determination of ΔH_i^*. Comparison of the activation parameters for a number of pentaammine-metal(III) complexes in various solvents shows that far from being typical, cobalt(III) is the only one of the metals listed to undergo reaction via an I_d mechanism.

CHAPTER 3

THE VOLUMES OF REACTION AND ACTIVATION FOR BROMIDE ANATION OF HEXAKIS(DIMETHYLFORMAMIDE)CHROMIUM(III) ION IN DMF

1. Introduction

The substitution reactions of aqueous $Cr(H_2O)_5X^{n+}$ ions have been studied extensively (see, for example, references 69-75). The assignment of mechanism in these reactions has been severely complicated by the occurrence of reaction pathways involving $[H^+]$, $[H^+]^{-1}$ and $[H^+]^{-2}$ dependences. In the rather extreme case of $Cr(H_2O)_5N_3^{2+}$ aquation, all three of these pathways and a hydrogen-ion independent pathway were found to occur[61]. In addition, because of the high dielectric constant of water and its ability to solvate small anions effectively through hydrogen-bonding, ion-pair formation constants are very small. Thus it is not possible to measure k_i and its associated activation parameters directly in aqueous solutions of $Cr(H_2O)_5X^{n+}$. To avoid these problems dipolar aprotic solvents such as DMSO and DMF have been used in some of the recent studies on Cr(III) ions.

Lo and Watts have studied the anation of $Cr(DMSO)_6^{3+}$ by N_3^-, NCS^- and Cl^- in DMSO and of $Cr(DMF)_6^{3+}$ by Cl^- in DMF[76]. In that work an I_d mechanism was assigned in spite of the variation in k_{an} for the various nucleophiles [2×10^{-5} s^{-1} (Cl^-), 2×10^{-4} s^{-1} (NCS^-) and 5-6 $\times 10^{-3}$ s^{-1} (N_3^-)] and in spite of the observation that $k_{an} = 100\ k_{ex}$ for $X^- = N_3^-$ in the $Cr(DMSO)_6^{3+}$ system. The authors suggest that differences in the free energies of the $\{Cr(DMSO)_6^{3+}, X^-\}$ and $\{Cr(DMSO)_6^{3+}, 2X^-\}$ aggregates relative to the free energy of free $Cr(DMSO)_6^{3+}$ could account for these observations. In a companion paper dealing with competitive anations

of the $Cr(DMSO)_6^{3+}$ ion in DMSO[77], the results of competition between NCS^- and Cl^- were found to be consistent with the results of anation by the two ions separately, and were again interpreted in terms of an I_d mechanism.

On the other hand, Carle and Swaddle[78] reported a ΔV^* for solvent exchange of $Cr(DMSO)_6^{3+}$ with DMSO of -11.3 cm^3 mol^{-1} which was taken as clear evidence of the operation of an I_a mechanism in this reaction. Furthermore, they stated that the anation data of Lo and Watts[76] were more consistent with an I_a mechanism than with an I_d one, since even in a solvent with bulky molecules like those of DMSO, exchange of solvent would not likely be blocked to such an extent as to allow an I_d anation by N_3^- to outpace solvent exchange by the factor of 100 observed. This latter argument would be valid only if no acceleration of the solvent exchange rate occurred upon ion-pairing of the complex. In the analogous $Cr(DMF)_6^{3+}$/DMF exchange reaction[17], k_{ex} was found to be slightly <u>decreased</u> by ion-pairing, and this is likely for the DMSO system too.

Lo and Swaddle[17,79] have studied the solvent exchange and anation reactions of $Cr(DMF)_6^{3+}$ in DMF in some detail. Variation in the value of ΔH_i^* with the nature of the anating ion, and a negative, pressure-independent value for ΔV_{ex}^* strongly suggest the operation of an I_a mechanism for both solvent exchange and anation. In addition to these two factors, k_i was found to be markedly dependent upon the nature of the entering ligand.

In the work to be described below, a study of the effect of pressure on the rate of bromide anation of $Cr(DMF)_6^{3+}$ in DMF was undertaken (21-22). The values of ΔV^* and ΔV, and their pressure-dependences, together

$$Cr(DMF)_6^{3+} + Br^- \rightleftharpoons \{Cr(DMF)_6^{3+}, Br^-\} \qquad 21$$

$$\{Cr(DMF)_6^{3+}, Br^-\} \longrightarrow Cr(DMF)_5Br^{2+} + DMF \qquad 22$$

with an estimate of the volume change associated with the ion-pairing pre-equilibrium were determined, to obtain evidence which would allow a clear choice to be made between the I_a and I_d mechanisms for anation of $Cr(solvent)_6^{3+}$ complexes.

Because of the incursion of a second reaction (presumably formation of $Cr(DMF)_4Br_2^+$) when the bromide anation is studied at Br^- concentrations high enough to ensure complete ion-pairing of the reactant complex, it was necessary to study the reaction by the rather tedious gravimetric method described in reference 17. In this way only the rate of disappearance of the starting material is monitored, and the second reaction does not interfere.

2. Experimental

2.1 Materials

DMF (Burdick and Jackson "Distilled in Glass"; $H_2O \leq 0.03\%$) was purified in the manner described in Chapter 2. Tetraethylammonium bromide (Baker) was recrystallized from DMF by the addition of ether. Baker Analyzed sodium tetraphenylborate was used as received, but that from Aldrich was first purified according to the method of Cox et. al.[80]

The perchlorate and tetraphenylborate salts of hexakis(dimethylformamide)chromium(III) were prepared from solid hexaaquochromium(III) perchlorate using the methods described by Lo and Swaddle[79]. Tetraethylammonium hexathiocyanatochromium(III) was prepared from the potassium salt as described in the same reference.

In the preparation of $[Cr(DMF)_5Br](BPh_4)_2$ a solution of 3 g $[Cr(DMF)_6](ClO_4)_3$ and 1.2 g tetrabutylammonium bromide in 30 mL DMF

was maintained at 110°C for six hours, then cooled in ice. A small volume of ether was added to reprecipitate unreacted starting material, which was removed by filtration. Following this an excess of ether was added to the filtrate to precipitate $Cr(DMF)_5Br^{2+}$ as the $BrClO_4$ salt[79]. This salt was dissolved in 25 mL DMF containing 2 drops of concentrated HCl. To the vigorously stirred solution was added dropwise a solution of 2 g $NaBPh_4$ in 50 mL water. Next, 100 mL water were added and the mixture stirred for five minutes. The crude tetraphenylborate salt was collected and washed thoroughly with methanol and ether. It was then dissolved in a minimum of DMF and reprecipitated by the addition of ethanol. The pure product was separated from the remaining $[Cr(DMF)_6](BPh_4)_3$ by repeated recrystallizations from acetone, in which the latter complex was much less soluble. Green $[Cr(DMF)_5Br](BPh_4)_2$ was precipitated from the acetone solution by the addition of ethanol, washed with ether, and dried on the vacuum line. Yield 0.7 g.

The spectrum of $[Cr(DMF)_5Br](BPh_4)_2$ in DMF showed absorptions at 639 nm and 448 nm (ε = 81.4 and 51.3 L mol^{-1} cm^{-1}, respectively) in excellent agreement with the values reported in the literature[17] (639 nm and 449 nm; ε = 81.6 and 52.1 L mol^{-1} cm^{-1}).

Tetraethylammonium tetraphenylborate was prepared by the addition of an aqueous solution of $NaBPh_4$ (1 g in 10 mL) to one of Et_4NBr (0.6 g in 10 mL). The crude product was washed with water followed by ether. It was then dissolved in 40 mL DMF and reprecipitated by the slow addition of ether. After washing with ether, the product was dried at 45°C under vacuum.

Analysis. Calculated for Et_4NBPh_4:
C 85.5, H 9.0, N 3.1;
Found: C 85.9, H 8.8, N 2.9.

2.2 Kinetics

The reaction of Et_4NBr with $[Cr(DMF)_6](ClO_4)_3$ in DMF was studied by the gravimetric method described previously[17]. Typically, solutions containing appropriate amounts of complex or Et_4NBr in DMF were separately equilibrated at the desired temperature, then mixed together to initiate the reaction. At suitable times, aliquots containing 7.58×10^{-5} mol of Cr(III) were withdrawn and cooled in ice. To each sample was added 8×10^{-5} mol $(Et_4N)_3[Cr(NCS)_6]$ in DMF to precipitate the unreacted starting material as $[Cr(DMF)_6][Cr(NCS)_6]$. After being allowed to stand at 0°C for at least 12 hours, the samples were filtered, washed thoroughly with acetone, dried under vacuum, and weighed (±0.05 mg).

Initially the atmospheric pressure runs were conducted in thermostatted, darkened Pyrex vessels from which samples were pipetted at intervals. Later runs were carried out in a similarly thermostatted, foil-covered syringe from which samples were run out via a long teflon needle.

The experiments under pressure were conducted using the high pressure assembly described in chapter 2. In some cases a type 304 stainless steel or teflon tube replaced the tantalum capillary described earlier.

2.3 Equilibrium Studies

In all experiments, equilibrium was approached from the $[Cr(DMF)_5Br]^{2+}$ side. The atmospheric pressure experiments were conducted in a 20 mm pathlength quartz optical cell thermostatted (±0.1°C) in an aluminum block located in the sample compartment of a Cary 17Hc spectrophotometer. A single experiment involved continuous monitoring of the sample

(λ = 640 nm) until equilibrium had been reached. In the other experiments, light was excluded from the sample except for short periods of time ($\sim$ 20 s) during which absorbance readings were taken. For the high pressure experiments the solution was contained in a sealed glass syringe which was loaded into the cavity of the high pressure assembly described above. After the desired length of time, the vessel was depressurized and the syringe removed and cooled to room temperature. The absorbance of the solution (640 nm) was then measured at that temperature.

2.4 Apparent Molal Volumes

The apparent molal volumes of the reactants and products were calculated from the densities of solutions of these compounds in DMF. The densities relative to dry N_2 and pure water were measured, using a Sodev model 02D vibrating tube densimeter coupled with a Systron-Donner 6150 frequency meter. The densimeter was thermostatted to ±0.001°C, allowing densities to be measured with a precision of ±4 ppm at 25°C and ±9 ppm at 50°C. All solutions were prepared by weight (±0.005 g) in a nitrogen-filled dry box.

3. Results

3.1 Kinetics

The anation data were initially fitted to an equation of the form given in 23 using a standard linear least squares program. In this equation, w_0, w_t and w_∞ refer to the weights of the precipitates from

$$\ln(w_t - w_\infty) = k_{an}t + \ln(w_0 - w_\infty) \qquad 23$$

samples taken at zero time, time t, and infinite time, respectively.

No attempt was made to measure w_∞, since for complete reaction $w_\infty = 0$. The reaction seemed to follow first-order kinetics over at least two half-lives at low pressures (≤ 200 MPa), but the plots of ln w_t vs. time were distinctly curved for runs at higher pressures. Equilibrium studies (see below) made it obvious that the reaction was only 98% complete at 0.1 MPa, and as little as 30% complete at 400 MPa. The data were therefore fitted to equation 24, in which w_e refers to the weights of precipitates from samples taken after equilibrium had been reached, and k is the pseudo-first-order rate coefficient for the approach to equilibrium. The value of w_e at each pressure was calculated

$$\ln(w_t - w_e) = kt + \ln(w_0 - w_e) \qquad 24$$

from the equilibrium constant at that pressure. A typical plot of $\ln(w_t - w_e)$ vs. time is given in figure 6.

From the k values obtained it was possible to calculate values of k_1 and k_{-1} using the relationships given in 25 and 26, where k_1 is the pseudo-first-order rate coefficient for anation of $Cr(DMF)_6{}^{3+}$ by Br^-, k_{-1} is the rate coefficient for solvolysis of $Cr(DMF)_5Br^{2+}$ and K is

$$k = k_1 + k_{-1} \qquad 25$$

$$K = \frac{k_1/[Br^-]}{k_{-1}} \qquad 26$$

the equilibrium constant.

Values of K, k, k_1 and k_{-1} for each pressure investigated are given in table 4. The pressure-dependences of ln k, ln k_1 and ln k_{-1} are shown graphically in figure 7. For the sake of clarity, only the average ln k, ln k_1 or ln k_{-1} has been shown for each pressure. The

significance of the solid curves shown in figure 7 will be discussed later.

The first few entries of table 4 show that atmospheric pressure runs conducted in a stoppered flask from which samples were withdrawn using a pipette, were ∿ 30% faster than those conducted in the syringe. The run with glass beads indicates that this was not a result of surface catalysis. It is probable that traces of moisture absorbed from the air when the vessel was unstoppered for withdrawal of the samples caused the acceleration.

3.2 Equilibrium Studies

The concentrations of $Cr(DMF)_5Br^{2+}$ $(c_0 - c_t)$, $Cr(DMF)_6{}^{3+}$ (c_t) and Br^- (c_t) present in any given solution at time t were calculated from the observed absorbance of the solution (A_t) together with the known molar absorptivities $(\varepsilon_{Cr^{3+}}, \varepsilon_{CrBr^{2+}})$ of the chromium(III) species in DMF according to equation 27, where b is the pathlength of the optical

$$A_t = \varepsilon_{Cr^{3+}} b c_t + \varepsilon_{CrBr^{2+}} b (c_0 - c_t) \qquad 27$$

cell used. The anions in the solution make no contribution to the absorbance of the solution at the wavelength used (640 nm).

Using the concentrations determined as above, in conjunction with the second-order rate coefficient for bromide anation of $Cr(DMF)_6{}^{3+}$, it was possible to calculate the concentration of each of the species present at equilibrium using the integrated rate expression (28)[81] for a reversible reaction involving a first-order forward and second-order back reaction.

$$\ln \frac{c_0{}^2 - c_e c_t}{(c_t - c_e) c_0} = k_{-1}' \left(\frac{c_0 + c_e}{c_0 - c_e} \right) t \qquad 28$$

Figure 6

$\ln(w_t - w_e)$ vs. time for
$Cr(DMF)_6^{3+} + Br^-$ system in DMF.
$[Cr(DMF)_6^{3+}] = 5.32 \times 10^{-3}$ m, $[Br^-] = 7.90 \times 10^{-2}$ m,
T = 84.99°C, P = 101.0 MPa.

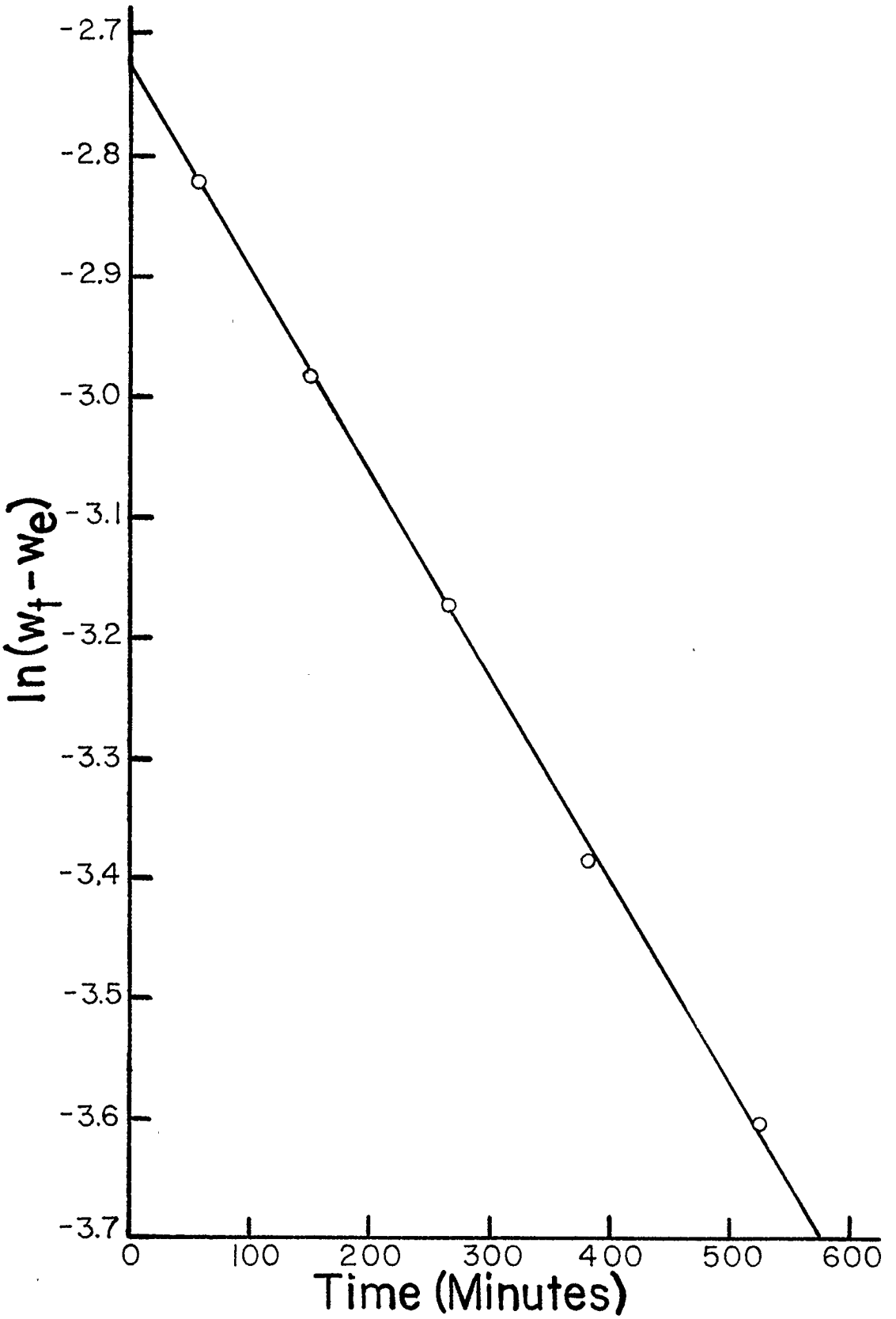

-2.7
-2.8
-2.9
-3.0
-3.1
-3.2
-3.3
-3.4
-3.5
-3.6
-3.7
ln(wt-we)
0
100
200
300
400
500
600
Time (Minutes)

TABLE 4. Pressure-Dependence of Equilibrium Constant and Rate Coefficients for

$Cr(DMF)_6^{3+} + Br^- \rightleftharpoons Cr(DMF)_5Br^{2+} + DMF$

in DMF. $[Cr(DMF)_6^{3+}] = 5.32 \times 10^{-3}$ m, $[Br^-] = 7.90 \times 10^{-2}$ m. T = 84.99°C

Pressure (MPa)	K (kg mol^{-1})	10^5 k (s^{-1})	10^5 k_1 (s^{-1})	10^5 k_{-1} (s^{-1})
0.1[a]	635.8	4.45±0.04	4.36	0.0869
0.1[a]	635.8	4.56±0.09	4.47	0.0890
0.1[b]	635.8	4.56±0.09	4.47	0.0890
0.1[c]	635.8	3.60±0.04	3.53	0.0703
0.1[d]	635.8	3.40±0.05	3.33	0.0663
0.1[d]	635.8	3.58±0.06	3.51	0.0698
24.5	476.2	3.16±0.06	3.08	0.0818
25.8	468.9	3.02±0.06	2.94	0.0793
48.7	357.4	2.90±0.06	2.80	0.0991
48.8	357.0	2.84±0.06	2.74	0.0972
99.6	195.5	2.65±0.05	2.49	0.161
101.0	192.3	2.81±0.04	2.64	0.173
148.4	109.6	2.72±0.08	2.44	0.281
150.4	107.1	2.75±0.09	2.46	0.290
199.5	59.83	2.54±0.06	2.10	0.443
201.2	58.64	2.56±0.04	2.10	0.454
251.5	32.30	2.84±0.08	2.04	0.799
252.6	31.88	2.84±0.06	2.03	0.807
301.6	17.84	3.58±0.08	2.09	1.48
305.0	17.13	4.00±0.04	2.30	1.70
354.5	9.528	4.84±0.23	2.08	2.76
354.6	9.528	4.99±0.34	2.14	2.85
400.3	5.536	6.60±1.04	2.01	4.59

a. Runs conducted in Pyrex flask. Surface area ∿ 15,700 mm^2.

b. Run conducted in Pyrex flask containing glass beads. Total surface area ∿ 63,200 mm^2.

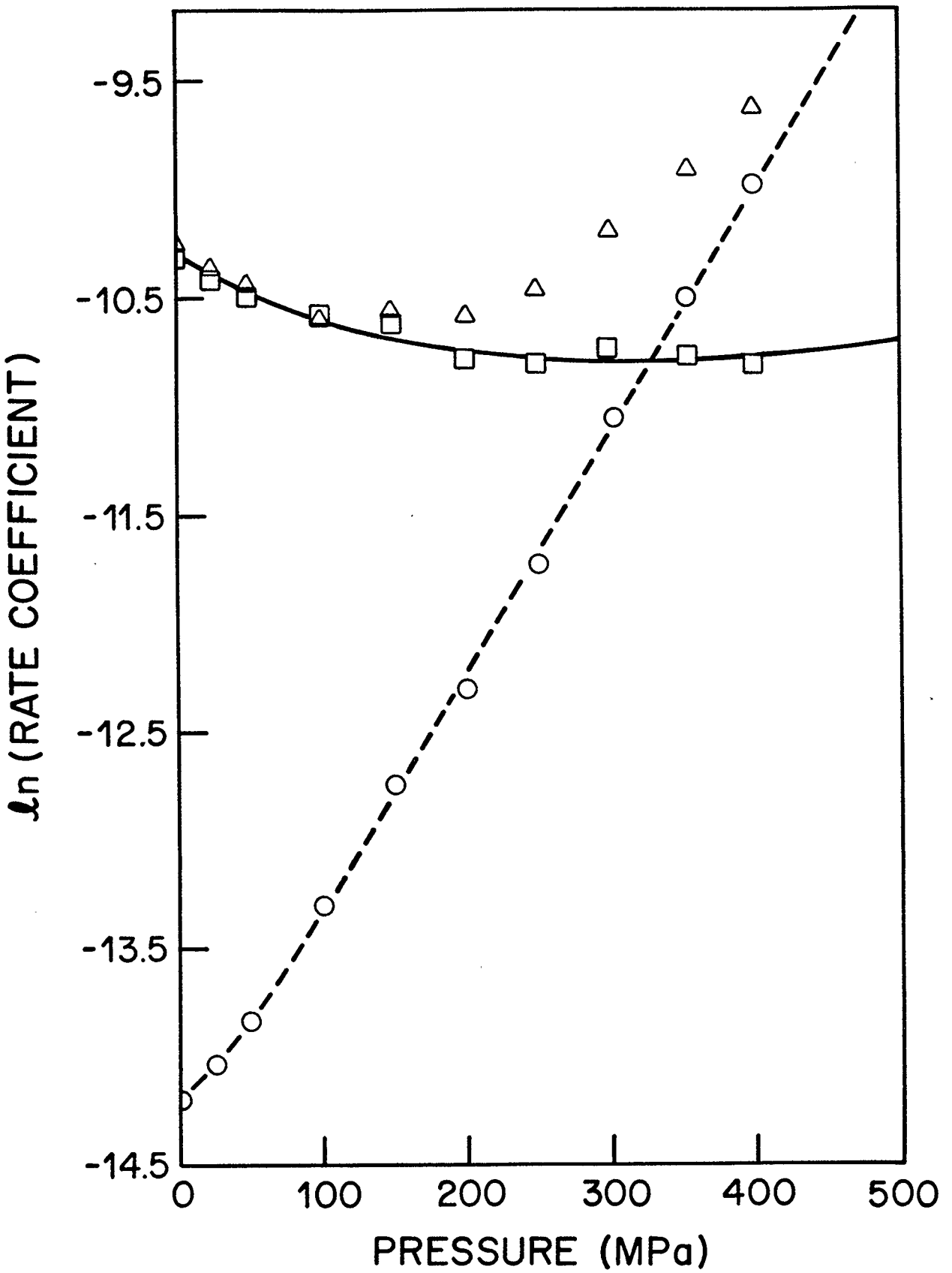
c. Calculated from ΔH^*, ΔS^* and data of reference 17.

d. Runs conducted in syringe.

Runs designated a, b, c not included in calculations or on figures following.

Figure 7

Pressure-Dependences of
ln kΔ, ln $k_1\square$, and ln k_{-1}O for
$Cr(DMF)_6{}^{3+} + Br^- \rightleftharpoons Cr(DMF)_5Br^{2+} + DMF$.


-9.5
-10.5
-11.5
-12.5
-13.5
-14.5
ln (RATE COEFFICIENT)
0
100
200
300
400
500
PRESSURE (MPa)

The equilibrium constants at different pressures were than calculated (29). The values of K so obtained are collected in table 5,

$$K = \frac{(c_0 - c_e)}{c_e^{\,2}} \qquad 29$$

together with the ΔV values calculated from them by means of equation 30, which assumes ΔV to be independent of pressure.

$$-\frac{\Delta V}{RT} = \frac{\Delta \ln K}{\Delta P} \qquad 30$$

In the atmospheric pressure experiments, equilibrium was reached much more rapidly when the sample was exposed to light continuously then when illuminated for only short periods of time. In the former experiment, equilibrium was reached in about 5 hours, while in the latter equilibration required about 3 days. The final absorbance was, of course, the same in both cases.

3.3 Apparent Molal Volumes

The densimeter operates on the principle that the period of vibration τ of a hollow reed, is dependent upon the density of the fluid with which the reed is filled. The relationship between the density of the fluid and the period of vibration is given by equation 31, where A and

$$d = A + K\tau^2 \qquad 31$$

K are instrumental calibration constants determined using two fluids of accurately known density (e.g. N_2 and H_2O).

Since densities of high precision (± a few ppm) are required in the calculation of apparent molal volumes, the density of the electrolyte solution is measured relative to that of a reference solution, usually

TABLE 5. Equilibrium Constants and Associated Volumes of Reaction for $Cr(DMF)_6^{3+} + Br^- \rightleftharpoons Cr(DMF)_5Br^{2+} + DMF$ at 85.0°C.

Pressure (MPa)	Extent of Anation at Equilibrium (%)	K.(kg mol^{-1})	ΔV (cm^3 mol^{-1})
0.1	98	575	----
0.1	98	575	----
201.0	82	57.3	34.2
201.0	80	51.7	35.7
350.5	42	9.12	35.2
350.5	47	11.2	33.7

pure solvent (32). By measuring the density of the reference before

$$d - d_0 = K(\tau^2 - \tau_0{}^2) \qquad 32$$

and after each sample, it is possible to eliminate errors arising from instrumental drift.

From the density and molality of the electrolyte solution, the density of the solvent d_0, and the formula weight of the electrolyte M_2, the apparent molal volume ϕ_V of the electrolyte can be calculated (33)[82].

$$\phi_V = \frac{1000\ (d_0 - d)}{m d_0 d} + \frac{M_2}{d} \qquad 33$$

The volume of reaction for the bromide anation of $Cr(DMF)_6{}^{3+}$ is then given by 34, where $\overline{V}^0(DMF)$ is the molar volume of DMF.

$$\begin{aligned} \Delta V &= \Sigma\phi_{V(\text{products})} - \Sigma\phi_{V(\text{reactants})} \\ &= \phi_V([Cr(DMF)_5Br](BPh_4)_2) + \phi_V(Et_4NBPh_4) + \overline{V}^0(DMF) \\ &\quad - \phi_V([Cr(DMF)_6](BPh_4)_3) - \phi_V(Et_4NBr) \qquad 34 \end{aligned}$$

Because of problems in thermostatting the densimeter, it was not possible to measure the apparent molal volumes of the reactants and products at 85°C. Measurements were therefore made at 25°C and 50°C, and the resulting volumes of reaction extrapolated to the higher temperature. The apparent molal volumes of the various species are listed in table 6. The concentrations used in these measurements were the same as those used in the kinetics experiments, except in the case of Et_4NBPh_4 at 50°C. At that temperature results obtained using 5.3×10^{-3} m solutions were poorly reproducible due to the small density change in-

TABLE 6. Apparent Molal Volumes for Species Involved in

$[Cr(DMF)_6](BPh_4)_3 + Et_4NBr \longrightarrow [Cr(DMF)_5Br](BPh_4)_2 + Et_4NBPh_4 + DMF.$

Compound	Concentration (mol kg^{-1})	ϕ_V (cm^3 mol^{-1})
T = 25°C		
Et_4NBPh_4	5.3×10^{-3}	422.2±0.5
Et_4NBr	7.9×10^{-2}	153.5±0.1
Et_4NBr[a]	7.9×10^{-2}	153.6
$[Cr(DMF)_6](BPh_4)_3$	5.3×10^{-3}	1272.1±0.3
$[Cr(DMF)_5Br](BPh_4)_2$	5.3×10^{-3}	927.0±0.2
DMF[b]	Molar Volume	77.4±0.1
$[Cr(DMF)_6](BPh_4)_3$ + Et_4NBr	5.3×10^{-3} 7.9×10^{-2}	1295.8±0.3
T = 50°C		
Et_4NBPh_4	5.3×10^{-3}	426.8±0.9
Et_4NBr	7.9×10^{-2}	151.9±2.0
$[Cr(DMF)_6](BPh_4)_3$	5.3×10^{-3}	1283.0±1.0
$[Cr(DMF)_5Br](BPh_4)_2$	5.3×10^{-3}	944.5±0.5
DMF[b]	Molar Volume	79.4±0.1
$[Cr(DMF)_6](BPh_4)_3$ + Et_4NBr	5.3×10^{-3} + 7.9×10^{-2}	1299.5±1.7

a. Value calculated from data in reference 83.

b. Calculated using density of pure solvent = 0.94406 g cm^{-3} at 25°C and 0.92002 g cm^{-3} at 50°C.

volved. Instead, solutions of higher concentration were used, and the average ϕ_V obtained taken to be the appropriate value for the concentration of interest.

From the apparent molal volumes given in table 6, ΔV values of 1.0±1.5 $cm^3\ mol^{-1}$ and 15.8±4.5 $cm^3\ mol^{-1}$ were calculated for 25°C and 50°C, respectively. Using a linear extrapolation, ΔV at 85°C and 0.1 MPa was calculated to be 36.4 $cm^3\ mol^{-1}$.

The volume change associated with the ion-pairing pre-equilibrium can also be estimated (35). For the first term, the solution used must

$$\Delta V_{IP} = \phi_V([Cr(DMF)_6](BPh_4)_3 \text{ in presence of } Et_4NBr) - \phi_V([Cr(DMF)_6](BPh_4)_3) - \overline{V}^0_{Br^-} \qquad 35$$

contain enough Et_4NBr to cause complete ion-pairing with the complex. A solution containing the same concentration of Et_4NBr, but without the complex, is used as a reference. Unfortunately, the partial molal volume of a single ion such as bromide cannot be measured directly. Various methods have been used for dividing the partial molal volumes of electrolytes in DMF into single ion values[83-85]. The values obtained for $\overline{V}^0_{Br^-}$ at 25°C range from 7 $cm^3\ mol^{-1}$ [84] to 33.3 $cm^3\ mol^{-1}$ [85]. These two extreme values notwithstanding, three different methods of calculation[83,85] give $\overline{V}^0_{Br^-} \sim 20\ cm^3\ mol^{-1}$ at 25°C. At infinite dilution, Avogadro's Number of unsolvated Br^- ions would be expected to occupy 18.7 $cm^3\ mol^{-1}$, assuming the radius of Br^- to be 1.95 Å. Since relatively small, spherical anions such as Br^- are expected to be poorly solvated in an aprotic solvent such as DMF[86], a $\overline{V}^0_{Br^-}$ not much different from 18.7 $cm^3\ mol^{-1}$ would be expected. Thus the value of 20 $cm^3\ mol^{-1}$ at 25°C seems reasonable. Furthermore the partial molal volume of an essentially unsolvated ion would not be expected to change significantly with temperature.

Thus $\bar{V}^0_{Br^-}$ at 50°C should also be ∿ 20 cm^3 mol^{-1}. On this basis, values of +4 cm^3 mol^{-1} and -4 cm^3 mol^{-1} would be obtained for ΔV_{IP} at 25 and 50°C, respectively. Considering the experimental error and the uncertainty in $\bar{V}^0_{Br^-}$, neither of these values is significantly different from 0. Thus ΔV_{IP} at 85°C is likely also approximately 0 cm^3 mol^{-1}.

4. Discussion

4.1 Volume of Reaction

The volume of reaction at 85°C was found to be 36.4, 35.0 and 34.4 cm^3 mol^{-1} at P = 0.1, 201, and 350 MPa, respectively. Since the experimental error associated with each of these values would be at least 2 cm^3 mol^{-1}, ΔV may be considered to be constant over the range of pressures studied. Thus the mean value of 35.3 cm^3 mol^{-1} was used in the calculation of the equilibrium constants and rate coefficients in table 4.

Although 35.3 cm^3 mol^{-1} seems a large volume change, in reality it corresponds to less than half (.43) of the molar volume of DMF at 85°C. Using Brummer's compression data (extrapolated to 350 MPa) it can be calculated that 0.43 $\bar{V}^0_{DMF}$ (and therefore ΔV) would be 5.4 cm^3 mol^{-1} larger at 0.1 MPa than at 350 MPa. This is within the experimental error on the values of ΔV listed above. Thus the use of a constant ΔV in the calculation of the equilibrium constants is seen to be a not unreasonable approximation.

Another point of interest is that ΔV is markedly temperature-dependent, being ∿ 35 cm^3 mol^{-1} more positive at 85°C than at 25°C. If dipole-dipole interactions are of importance in the solvation of the product complex in DMF (see section 4.3), the greater degree of randomness in the bulk solvent arising from the increased thermal motion may

result in slightly less efficient solvation of this complex, and thus the release of slightly more solvent from the coordination spheres during reaction at the higher temperature. In addition, the molar volume of DMF at 85°C is about 5 $cm^3\ mol^{-1}$ larger than at 25°C, which would account for part of the temperature dependence of ΔV.

4.2 Pressure-Dependence of the ΔV^* Values

4.2.1 $\Delta V_1{}^*$

As shown in figure 7, the ln k_1 vs. pressure plot is distinctly curved at low pressures. Thus the linear function (equation 12) given in chapter 1 is clearly not adequate for the purpose of calculating ΔV^* in this case, since ΔV^* is significantly pressure-dependent. Various functions have been suggested as being suitable for the fitting of non-linear pressure/rate data. Hyne et. al.[88] have paid particular attention to this question, but mostly from the point of view of reactions other than those of complex metal ions. In general they found the data to be best fitted to a second-order power series in P (equation 36). In this equation, k_0 and $\Delta V_0{}^*$ refer to the rate coefficient and volume of

$$\ln k = \ln k_0 - \frac{\Delta V_0{}^*}{RT} P - \frac{(\partial \Delta V^*/\partial P)_T}{2RT} P^2 \qquad 36$$

activation at zero pressure, and $(\partial \Delta V^*/\partial P)_T$ allows for the pressure-dependence of ΔV^*.

Hyne and co-workers[88a] found that for the one complex metal ion reaction they tested, namely the base hydrolysis of $Co(NH_3)_5Br^{2+}$, Benson and Berson's[89] modification (37) of Tait's empirical equation for the compression of liquids gave a slightly better fit. In this

$$\frac{\ln (k/k_0)}{P} = A + BP^{0.523} \qquad 37$$

equation, A allows calculation of ΔV_0^* as above, and B is a measure of the change in compressibility of bulk solvent with pressure. It was thought[88a] to be surprising that this equation fitted the data in an aqueous system so well, since the exponent 0.523 was derived using compression data for organic liquids, and should not apply in water.

Swaddle et. al.[66] found that an somewhat different modification of the Tait equation (38) gave a marginally better fit of the pressure-dependence of the rate coefficient for aquation of several $Co(NH_3)_5X^{2+}$ complexes than did the quadratic. In this equation x is defined as the

$$\ln k = \ln k_0 - \frac{\Delta V_0^*}{RT} P - \frac{\overline{V}_s^0 x \rho}{2.303\ RT} [(\pi + P)\ln(1 + P/\pi) - P] \qquad 38$$

increase in the number of solvent molecules solvating the complex as it goes from the initial state to the transition state, $\overline{V}_s^0$ is the molar volume of the solvent, and ρ and π are constants which may be determined from compression data for the solvent of interest using equation 39.

$$\frac{(V_0 - V_\rho)}{V_0} = \rho \log_{10} (1 + P/\pi) \qquad 39$$

Fairhurst and Swaddle[11] found that the pressure-dependence of the rate data for aquation of $Ru(NH_3)_5Cl^{2+}$ was best fitted using a cubic equation (40). The constants C and D represent the first and second-

$$\ln k = \ln k_0 - \frac{\Delta V_0^*}{RT} P + CP^2 + DP^3 \qquad 40$$

order pressure-dependences of ΔV^*. The data cited in the reference were deemed too imprecise to warrant consideration of the numerical values of these latter two parameters.

The failure of equation 38 to fit the data for the $Ru(NH_3)_5Cl^{2+}$ aquation was ascribed to the formation of a long-lived seven-coordinate intermediate (A-mechanism), which would make a contribution to the curvature of the ln k vs. pressure plot. Equation 38 is derived on the assumption that all of the curvature is due to solvational change (I-mechanism). A similar failure of equation 38 might be expected for a D-mechanism, in which a long-lived five-coordinate intermediate would be formed. Thus, it may be possible to distinguish between an A- or D-type mechanism and an I-mechanism on the basis of whether or not the pressure-dependence of ΔV^* can be adequately described in terms of solvational changes only.

Asano and leNoble[90] have suggested an equation of the form given in 41. This is merely a special case of equation 40, in which the CP^2 term

$$\ln k = A + BP + DP^3 \qquad 41$$

is of negligible importance relative to the others.

The data for the bromide anation of $Cr(DMF)_6{}^{3+}$ in DMF are unfortunately not particularly precise, especially at high pressures where the "correction" arising from the reverse (solvolysis) reaction is comparable in size to the anation rate coefficient. Thus, although the value of $\Delta V_0{}^*$ obtained should be quite reliable since it is determined mainly by the low pressure data which require little adjustment to account for solvolysis, any parameter describing the curvature of the plot must be regarded as being only approximate. It is also to be expected that the precision of any data fit will be lower than is usual in such studies, because of the scatter in the high pressure data.

The data were fitted to the linear and quadratic functions (equations

12 and 36) and to the modified Tait equation (38). In addition, ΔV_0^* was determined from the slope of a line drawn tangentially to a hand-drawn curve of the low pressure data. The results of these treatments are given in table 7.

The solid curve drawn through the k_1 data in figure 7 is the calculated curve for the modified Tait fit of all the data. As can be seen in the figure, this function underestimates the curvature at the low pressure end of the curve, and thus ΔV_0^*. This problem is partially corrected by excluding the 150 MPa data which seem to be anomalously high. It is clear from table 7 that the quadratic underestimates the curvature of the low pressure data to an even greater extent, and that the linear function gives a very poor fit indeed, as was to be expected. The graphical method for determining ΔV_0^* gives no weight to the high pressure data and thus probably overestimates the curvature at low pressures to some extent. It would seem, therefore, that the "true" value of ΔV_0^* lies between 11.5 and 15 $cm^3\ mol^{-1}$, with a value near 13 $cm^3\ mol^{-1}$ being most probable.

The modified Tait equation, whether the data at 150 MPa are included or not, gives a value of x near -1. Thus approximately 1 mole of DMF is released by the complex on going to the transition state. Because of the large molar volume of DMF, this gives rise to a considerable amount of curvature in the ln k_1 vs. pressure plot.

As is shown in figure 7, the modified Tait equation predicts that the slope of the ln k_1 vs. pressure plot should become positive at pressures above approximately 350 MPa. This occurs because the compressibility of the bulk solvent is becoming relatively small at these pressures. If the reaction could be followed to high enough pressures, the

TABLE 7. Least Squares Analysis of k_1 Data from Table 4.

Function	$10^5 (k_1)_0$ (s^{-1})	$(\Delta V_1^*)_0$ ($cm^3\ mol^{-1}$)	Other Parameters	Correlation Coefficient R^2
Linear	3.02	3.6	------	0.8010
Quadratic	3.29	8.9	$(\partial\Delta V^*/\partial P)T = -2.82 \times 10^{-2}$ $cm^3\ mol^{-1}\ MPa^{-1}$	0.9354
Modified Tait[a,b]	3.34	11.5	x = -0.95	0.9419
Modified Tait[b,c]	3.36	12.6	x = -1.08	0.9540
Tangent to Hand-Drawn Curve	3.42	15	------	------

a. All k_1 data used.

b. $\rho = 0.2091$, $\pi = 81.61$ MPa. Calculated from compression data in ref. 87.

c. Data for 150 MPa excluded.

compressibility of the bulk solvent would become almost as small as it is for the solvent in the first and second coordination spheres, at which point $\Delta V_s^* \sim 0$. The slope of the ln k_1 vs. P curve should thus be a direct measure of ΔV_b^* at these pressures. For the reaction under discussion, the Tait equation predicts a negative ΔV_b^*.

It is unfortunate that the solvolysis reaction becomes dominant at these very high pressures, and would therefore prevent the testing of this prediction, even if suitable apparatus were obtained. Such behavior is not likely to be detectable in aqueous systems either, because the value of the π-parameter of the Tait equation is almost 300 MPa for water even at 85°C[91]. This means that pressures greatly exceeding 400 MPa would be needed to cause the third term in the Tait equation to overwhelm the second.

4.2.2 ΔV_{-1}^*

The curve drawn through the ln k_{-1} vs. pressure data in figure 7 is purely empirical, and was hand-drawn to suit the data. No other treatment of the apparent curvature was justified, since the solvolysis data are rather imprecise, especially at low pressures where solvolysis accounts for less than 10% of the rate of approach to equilibrium.

A line drawn tangentially to the curve at zero pressure yields a $(\Delta V_{-1}^*)_0$ value of -20 $cm^3\ mol^{-1}$. This is a direct result of the fact that ΔV was used to effect the separation of k into its k_1 and k_{-1} components. If the ΔV_0^* values for both reactions are calculated using the method of tangents, so as to take full account of the curvature at low pressures, then $(\Delta V_1^*)_0 - (\Delta V_{-1}^*)_0$ will be exactly equal to the value of ΔV used to calculate k_1 and k_{-1} in the first place. Since $(\Delta V_1^*)_0$ is obtained from the low pressure data which is only slightly affected by the failure of

the anation reaction to reach completion, it should be quite reliable. Any error in the value of ΔV used will be present in almost its entirety in the value of $(\Delta V_{-1}^{*})_0$. For this reason, -20 cm^3 mol^{-1} must be regarded as being only an approximate value.

4.3 Solvational Changes

The volume changes associated with the various stages in the bromide anation of $Cr(DMF)_6^{3+}$ are summarised in table 8, and shown schematically in figure 8. One of the more striking features of this particular system is the smallness of the solvational changes involved. There is apparently no change in the number of molecules of DMF solvating the complex as the formation of the ion-pair occurs, and a loss of only one molecule occurs on going to the transition state. The volume change occurring in going from the transition state to the products amounts to only about 25% of the molar volume of DMF at 85°C.

In the aquation of various $Co(NH_3)_5X^{2+}$ species, the solvating of the departing anion appears to be largely responsible for the observed volume changes[66]. In water small anions are very well solvated because of the possibility of hydrogen-bonding between water and the anion, and thus the number of molecules of water involved may be quite large. In DMF and other aprotic solvents, on the other hand, anions are very poorly solvated[92]. Thus in the bromide anation of $Cr(DMF)_6^{3+}$ in DMF, desolvation of the bromide ion on inner- or outer-sphere complex formation may be, and apparently is, insignificant.

The other potential sources of solvational change are the complex cations. Although cations are expected to be well solvated in a dipolar aprotic solvent such as DMF, a very large ion such as $Cr(DMF)_6^{3+}$ may not be. $Cr(DMF)_6^{3+}$ has no acidic protons and thus cannot hydrogen bond to the oxygen atom in DMF. Furthermore, the complex has no dipole moment

TABLE 8. Volume Changes Associated with

$Cr(DMF)_6^{3+} + Br^- \rightleftharpoons \{Cr(DMF)_6^{3+}, Br^-\} \longrightarrow Cr(DMF)_5Br^{2+} + DMF$

Temperature (°C)	ΔV_{IP} ($cm^3\ mol^{-1}$)	$\Delta V_1{}^*$ ($cm^3\ mol^{-1}$)	ΔV ($cm^3\ mol^{-1}$)
25	+3.7	---	+1.0
50	-3.5	---	+15.8
85	0[a]	+13	+35.3

a. Estimated from data at lower two temperatures.

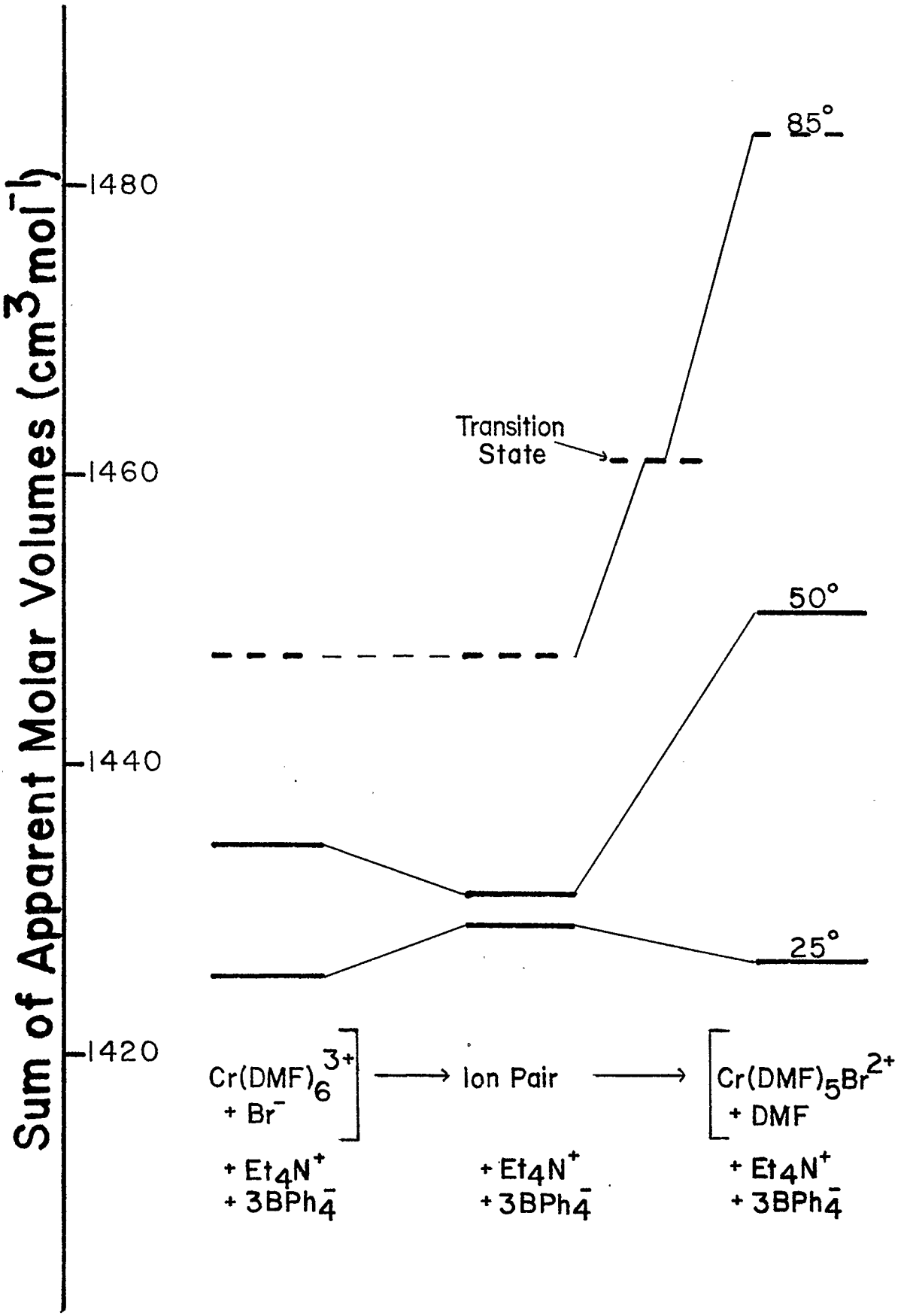
Figure 8

Volume Changes Associated with

$$Cr(DMF)_6^{3+} + Br^- \rightleftharpoons \{Cr(DMF)_6^{3+}, Br^-\}$$

$$\longrightarrow Cr(DMF)_5Br^{2+} + DMF.$$

———— Directly Measured; -------- Extrapolated From Data at Lower Temperatures.


Sum of Apparent Molar Volumes (cm3 mol-1)
1480
1460
1440
1420
85°
50°
25°
Transition State
Cr(DMF)6 3+
+ Br-
+ Et4N+
+ 3BPh4-
Ion Pair
+ Et4N+
+ 3BPh4-
Cr(DMF)5Br 2+
+ DMF
+ Et4N+
+ 3BPh4-

with which to engage in dipole-dipole interactions with the solvent, and its +3 charge is dispersed over a very large volume, so that ion-dipole interactions may not be strong either. Upon formation of the ion-pair or product, any further weakening of the already feeble ion-dipole forces may be partially or wholly compensated for by the generation of a dipole moment in the complex. Thus little solvational change would be expected from these sources either.

4.4 Assignment of Mechanism

The volume parameters obtained are consistent with the assignment of an I_a mechanism to the bromide anation of $Cr(DMF)_6{}^{3+}$ in DMF. Although the entry of the Br^- ligand into the first coordination sphere of chromium would make a negative contribution to ΔV^*, the concomitant lengthening of the Cr-DMF bonds, especially that to the leaving group, might outweigh this contribution giving a net positive value for ΔV^*. Such an overpowering of the bond-making contribution by the bond-breaking one would likely not occur in water, since the molar volume of the leaving group (H_2O) is about the same as that of the anion (Br^-), nor would it be likely in solvent exchange in DMF where the volumes of the entering and leaving groups are equal. In the present instance, however, the molar volume of the leaving group is about four times that of the attacking group.

The one mole of DMF released on going to the transition state (x in the Tait equation) would thus be partially a result of the expulsion of solvent from the second coordination sphere of the complex in order to make room for the leaving group there, and partially a result of desolvation of the complex as its charge began to decrease. The remaining volume increase on going to the products would also result from desolva-

tion of the complex.

The value x = -1 obtained from the Tait equation is suggestive of a D-mechanism. The loss of one DMF molecule on going to the transition state would correspond to the formation of the five-coordinate intermediate without change in the degree of solvation of the complex. Slight desolvation of the complex would then occur on going to the products. The lack of volume change on formation of the ion-pair might indicate that no ion-pair had formed. The zero-order dependence on $[Br^-]$ at high concentrations would then be attributed to the consumption of the five-coordinate intermediates as rapidly as they were formed.

The arguments given in the last paragraph notwithstanding, there are two aspects of the high-pressure data which strongly suggest that the I_a assignment is the correct one. Firstly, if a D-mechanism were operative, the rate-determining step (equation 42) would be the same as

$$Cr(DMF)_6^{3+} \longrightarrow Cr(DMF)_5^{3+} + DMF \qquad 42$$

that for solvent exchange. For this reason the same value of ΔV_0^* would be obtained for both the anation and solvent exchange reactions. The formation of ion-pairs would not invalidate the last statement, since ΔV_{IP} was shown to be approximately zero. The observed values for ΔV_{ex}^* and $(\Delta V_1^*)_0$, being -6.3±0.2 $cm^3\ mol^{-1}$ (pressure-independent)[79] and +13±2 $cm^3\ mol^{-1}$ (pressure-dependent) respectively, are clearly not identical. In contrast, Palmer and Kelm[93] have found the ΔV^* values for the anation reactions of $Co(CN)_5OH_2^{2-}$ by Br^-, I^- and NCS^- to be the same within the experimental error, consistent with the formation of a common long-lived, five-coordinate intermediate in all three cases. The reactions of the acidopentacyanocobaltate(III) complexes have generally

been regarded as being classic examples of the D-mechanism.

The second line of evidence which suggests that an I_a-mechanism, rather than a D-mechanism, is operative in the Br^- anation of $Cr(DMF)_6{}^{3+}$ is the acceleration in rate predicted by the Tait equation to occur at high pressures. It is unfortunate that the actual data do not extend to high enough pressures to confirm this acceleration, but the occurrence of a zero slope for pressures between 200 and 400 MPa strongly suggests that the slope of the ln k_1 vs. pressure plot would become negative at still higher pressures. It is difficult to envision a negative ΔV^* arising from a D-mechanism, especially at pressures under which solvational contributions to the volume change would be negligible.

5. Conclusions

The bromide anation of $Cr(DMF)_6{}^{3+}$ in DMF was found to be a reversible process, with the reactants being favoured at pressures greater than about 330 MPa. In contrast to aqueous systems, the reaction involved only minor solvational changes throughout. The volume parameters obtained for the forward reaction confirmed the operation of an I_a-mechanism in the reactions of $Cr(DMF)_6{}^{3+}$ in DMF.

CHAPTER 4

VOLUME PARAMETERS IN MECHANISTIC STUDIES OF ACIDOPENTAAMMINECOBALT(III) COMPLEXES IN AQUEOUS SOLUTIONS

1. Introduction

The reactions of acidopentaamminecobalt(III) species have been among those most intensively studied by inorganic solution kineticists. These complexes have been firmly established as reacting by dissociatively activated pathways, with I_d mechanisms predominating in acidic media[3,4a]. Because they are so well understood, this series of complexes serves as a good testing ground for new approaches to mechanistic studies[19], and as a source of more detailed information on older approaches.

In the work to be described below, the aquation of $Co(NH_3)_5SO_4^+$ (equation 43) has been used to determine the effect of changes in temperature on ΔV_0^*. This reaction was chosen because the ΔV_s^* contribution to ΔV_0^*, which would be expected to account for most of the temperature-dependence of ΔV_0^*, is particularly large in this case. In addition,

$$Co(NH_3)_5SO_4^+ + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + SO_4^{2-} \qquad 43$$

the effect of pressure on the rate of the acid-catalysed pathway[50,94] (equations 44 and 45) has been studied.

$$Co(NH_3)_5SO_4^+ + H^+ \rightleftharpoons Co(NH_3)_5HSO_4^{2+} \qquad 44$$

$$Co(NH_3)_5HSO_4^{2+} + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + HSO_4^- \qquad 45$$

After this work had been begun a paper by van Eldik *et. al.*[55] reported a value of ΔV^* for the uncatalysed aquation of sulphatopentaamminecobalt(III) at 60°C. The value obtained by these authors was markedly different from that obtained by Jones and co-workers[66] at 25°C, and was

attributed to the difference in temperature. In the discussion to follow, an alternative explanation will be given for this discrepancy.

Also to be discussed below are some results published in a paper by Palmer and Kelm[19] in which a volume profile approach was used to distinguish between I_d and I_a mechanisms in aquation reactions of cobalt(III) and chromium(III) pentaammine complexes. It was suggested by these authors that in an I_d mechanism the transition state would closely resemble solvated $M(NH_3)_5{}^{3+}$ and X^{n-} species. They argue, therefore, that if such a mechanism applies, a constant value of the partial molal volume of $M(NH_3)_5{}^{3+}$ should be obtained for aquation reactions of a whole series of complexes $M(NH_3)_5X^{(3-n)+}$. This partial molal volume can be calculated using equation 46, where $\overline{V}^{\circ}_{M(NH_3)_5{}^{3+}}$, $\overline{V}^{\circ}_{M(NH_3)_5X^{(3-n)+}}$, and $\overline{V}^{\circ}_{X^{n-}}$ are the

$$\overline{V}^{\circ}_{M(NH_3)_5{}^{3+}} = \overline{V}^{\circ}_{M(NH_3)_5X^{(3-n)+}} + \Delta V^{*} - \overline{V}^{\circ}_{X^{n-}} \qquad 46$$

partial molal volumes of $M(NH_3)_5{}^{3+}$, $M(NH_3)_5X^{(3-n)+}$, and X^{n-} respectively, and ΔV^{*} is the volume of activation for the aquation reaction. Palmer and Kelm found that a constant $\overline{V}^{\circ}_{M(NH_3)_5{}^{3+}}$ value was obtained for M = Co(III) but not for M = Cr(III), and interpreted this in terms of a change in mechanism from I_d to I_a on going from Co(III) to Cr(III). Rather curiously, it was necessary to assume that $\overline{V}^{\circ}_{H_2O} = 0$ for the cobalt(III) series of complexes, but not for the chromium(III) series. This was also found to be the case when ΔV for the aquation was calculated (equation 47).

$$\Delta V_{calc.} = \overline{V}^{\circ}_{M(NH_3)_5OH_2{}^{3+}} + \overline{V}^{\circ}_{X^{n-}} - \overline{V}^{\circ}_{M(NH_3)_5X^{(3-n)+}} - \overline{V}^{\circ}_{H_2O} \qquad 47$$

In the present work, the partial molal volumes of several of the complexes used by Palmer and Kelm have been re-determined. An explanation will be given as to why the results obtained in the present work for some of the cobalt(III) complexes differ from those found in the earlier study.

2. Experimental

2.1 Materials

Baker Analyzed Perchloric Acid (70-72%) was used as received. Lithium perchlorate trihydrate was prepared from Baker Analyzed $HClO_4$ and Li_2CO_3, and recrystallized from water. Sodium perchlorate monohydrate (Fisher) was recrystallized from water. Distilled water was passed through Barnstead de-mineraliser and organic removal cartridges before use.

$[Co(NH_3)_6](ClO_4)_3$, $[Co(NH_3)_5OH_2](ClO_4)_3$, and $[Co(NH_3)_5X](ClO_4)_2$ ($X^- = Cl^-$ and Br^-) were from earlier preparations[66,95]. The chloro- and bromo- complexes were recrystallised from perchloric acid before use. $[Cr(NH_3)_5OH_2](NO_3)_3 \cdot NH_4NO_3$ [96], $[Cr(NH_3)_5OH_2](NO_3)_3$ [96], $[Cr(NH_3)_5OH_2](ClO_4)_3$ [97], $[Cr(NH_3)_5Cl]Cl_2$ [98] and $[Cr(NH_3)_5Cl](ClO_4)_2$ [99] were prepared by standard methods. $[Co(NH_3)_5SO_4]ClO_4$ was prepared from $[Co(NH_3)_5CO_3]NO_3$ [100] using the methods described in references 66 and 101; the results of the kinetic experiments were not dependent upon which of the two methods was used. The purity of each of the complexes was confirmed by passing an aqueous solution of the complex onto a column of Dowex 50W-X8 in the H^+ form, and titrating the liberated acid using standard NaOH. The identity of the $[Co(NH_3)_5SO_4]ClO_4$ was also confirmed spectrophotometrically[66].

2.2 High Pressure Apparatus

The high pressure experiments at 35°C were conducted in the apparatus described in chapter 2, with the samples being withdrawn from the syringe via a teflon tube.

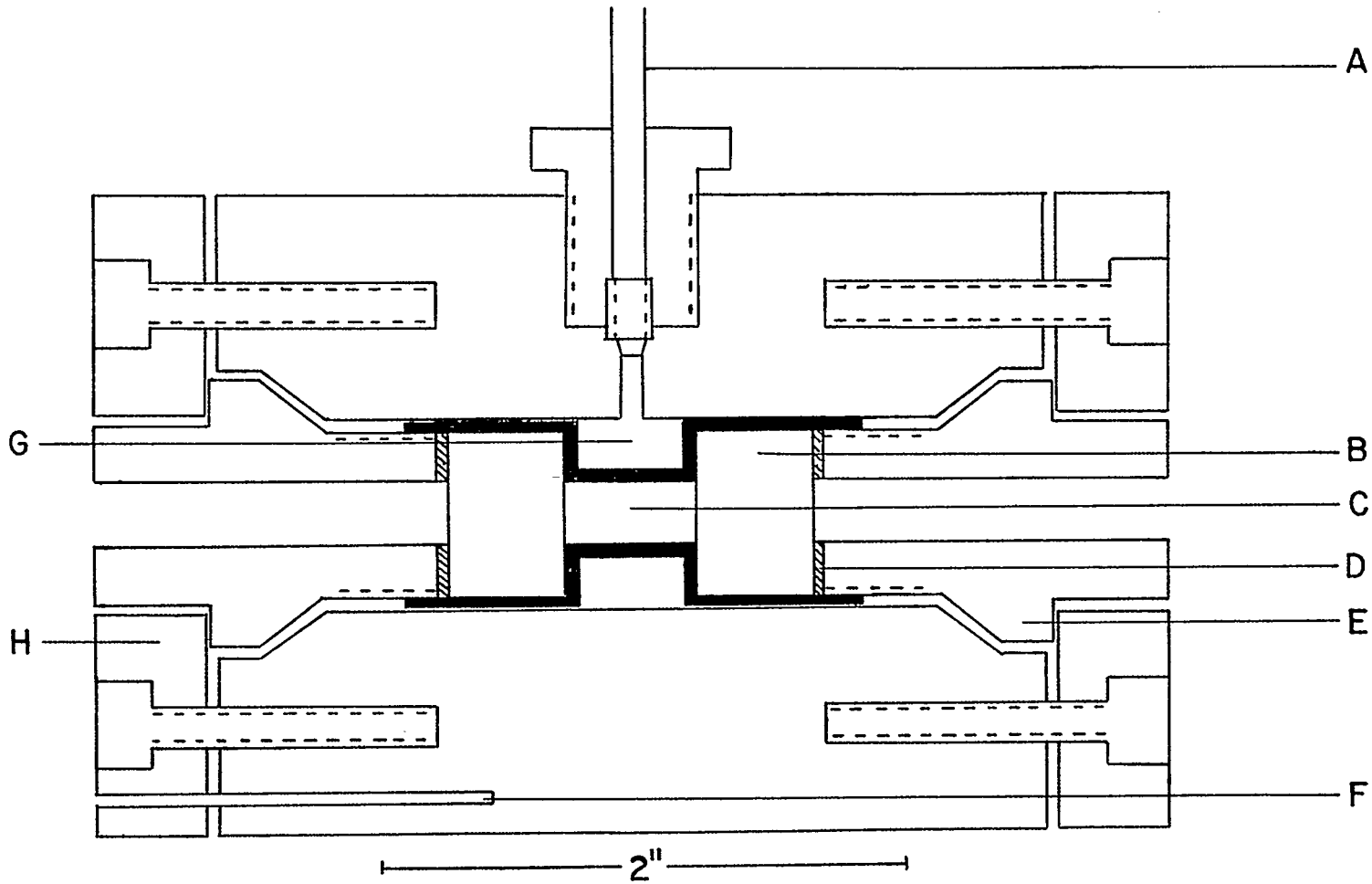
The experiments at 55°C were performed using an optical cell (figure 9) similar to that described by Franck *et. al.*[102]. The reaction solution is contained in the teflon "bellows", which deforms when external pressure is applied to it, thereby transmitting the pressure to the solution. Steel caps (not shown) surround those parts of the teflon bellows which hold the sapphire windows. The conical plugs are threaded into these caps, and bear down upon the windows in such a way as to seal the solution into the cavity between the windows. Also not shown are two steel spacers which prevent the two ends of the teflon bellows from twisting in opposite directions and tearing during assembly. The windows are transparent to visible and ultraviolet radiation, thus allowing *in situ* monitoring of the reaction. An insulated jacket through which water is circulated from a controlled temperature bath was used to thermostat the cell. An Atkins model 3H01 thermistor thermometer, calibrated frequently against mercury thermometers, was used to monitor the temperature.

2.3 Kinetics

A weighed amount of $[Co(NH_3)_5SO_4]ClO_4$ was dissolved in a known volume of water, then made up to the desired acidity and ionic strength using stock solutions of $HClO_4$ and $LiClO_4$. Atmospheric pressure experiments were performed by withdrawing samples from darkened, stoppered Pyrex vessels maintained at the appropriate temperature (±0.01°C) by means of a Sargent Thermonitor model ST constant temperature bath. The

Figure 9

Franck Optical Cell
A. Connection to Pump and Gauge,
B. Sapphire Window, C. Teflon "Bellows",
D. Polyethylene O-Ring, E. Steel
Cone, F. Thermistor Well, G. Pressurising
Fluid, H. End-Plate


A
B
C
D
E
F
G
H
2"

samples were quenched in ice, and maintained at 0°C until one hour before measurement of the optical absorbances, at which time they were allowed to warm up to room temperature. The absorbances of the samples were monitored at 280 nm using a Cary 17Hc spectrophotometer.

The high pressure runs were conducted in the two assemblies described above. The samples withdrawn at 35°C were handled in the same way as those from atmospheric pressure runs. The reaction at 55°C was monitored *in situ*.

2.4 Density Measurements

The density measurements were carried out using the instrumentation described in chapter 3. All solutions were prepared volumetrically, except those used in the attempts at determining the ΔV for aquation of $[Co(NH_3)_5SO_4]ClO_4$ in 0.95 m ionic strength solution, which were prepared by weight.

The volume of reaction for aquation of $Co(NH_3)_5SO_4^+$ was determined by measuring the densities of two aliquots of a solution of the complex, one of which had been base hydrolyzed, then reacidified. The other aliquot was treated with the same volumes of acid and base, but in this case the acid was added first to prevent the base hydrolysis. The reference solution used also contained the same amounts of acid and base, but no complex.

3. Results

3.1 Kinetics

The aquation data were fitted to the integrated rate expression for a first-order reaction (equation 23, chapter 3 with absorbances used in place of weights). The absorbances at infinite time were measured in the case of runs involving the sampling technique, but calculated for

runs performed in the optical cell. The reaction followed first-order kinetics over at least two half-lives at both temperatures studied. A typical plot of ln $(A_t - A_\infty)$ vs. time for a run at 35°C is given in figure 10. Similar plots were obtained for runs at 55°C. The acid- and pressure-dependences of the observed rate coefficient k_{obs} at 34.99°C and 54.99°C are shown by the data listed in tables 9 and 10, respectively.

A plot of k_{obs} vs. $[H^+]$ at any given temperature and pressure yields a straight line of the form given in equation 48 [50], where k_{aq} and k_H

$$k_{obs} = k_{aq} + k_H K_H [H^+] \qquad 48$$

are the first-order and second-order rate coefficients for spontaneous and acid-catalysed aquation, respectively and K_H is the acid association constant of $Co(NH_3)_5SO_4^+$ (equation 44). A typical plot of k_{obs} vs. $[H^+]$ is given in figure 11. Values of k_{aq} and k_H' (= $k_H K_H$) obtained from linear least squares treatments of the data for various pressures are given in table 11. The pressure-dependences for these rate coefficients are shown graphically in figures 12 and 13.

3.2 Density Measurements

3.2.1 ΔV for Uncatalysed Aquation of $Co(NH_3)_5SO_4^+$

Attempts at measuring ΔV in solutions of ionic strength 0.95 m, as used in the kinetic experiments, failed due to the large error introduced into the density measurements if even a 0.01 g excess of the inert electrolyte stock solution were added to one of the samples. Consequently, ΔV was measured at an ionic strength of about 0.08 m. At 55°C this approach also failed, apparently due to reaction of the cobalt solutions with the stainless steel vibrating tube of the densimeter.

Figure 10

Typical plot of ln $(A_t - A_\infty)$
<u>vs</u>. time for aquation of $Co(NH_3)_5SO_4^+$.
$T = 34.99°C$, $P = 149.6$ MPa, $[Co(NH_3)_5SO_4^+]$
$= \sim 6 \times 10^{-4}$ m, $[H^+] = 0.0996$ m.

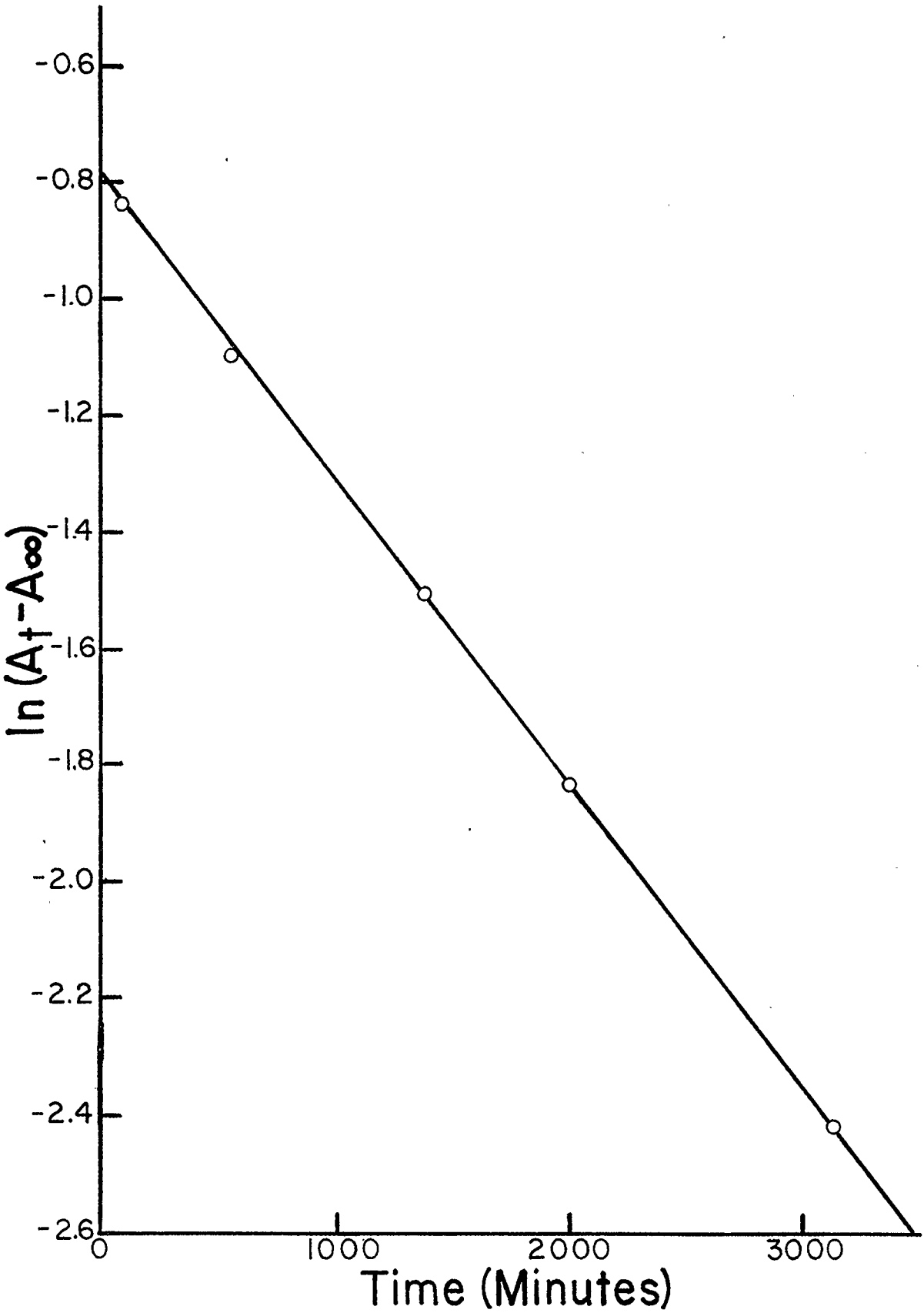

-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
-2.6
ln (At-A∞)
0
1000
2000
3000
Time (Minutes)

TABLE 9. $[H^+]$- and Pressure-Dependences of k_{obs} for $Co(NH_3)_5SO_4^+ + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + SO_4^{2-}$ at 34.99°C[a].

Pressure (MPa)	$[H^+]$ (mol kg^{-1})	$10^6\ k_{obs}$ (s^{-1})
0.1	0.0961	3.97±0.02
	0.0961	3.98±0.03
	0.1442	4.44±0.04
	0.4807	6.29±0.02
	0.9614	9.56±0.09
25.5	0.0961	4.90±0.01
	0.1442	5.03±0.05
	0.4979	7.57±0.07
	0.9614	10.4 ±0.3
50.0	0.1442	5.82±0.10
	0.4979	8.24±0.11
	0.9614	11.3 ±0.4
75.6	0.1009	6.22±0.01
	0.4979	9.11±0.16
	1.0090	12.6 ±0.5
99.1	0.1009	7.06±0.13
	0.1514	7.27±0.12
	0.5045	10.0 ±0.2
	0.9957	13.8 ±0.1
149.6	0.0996	8.62±0.04
	0.1494	8.99±0.14
	0.4979	11.8 ±0.2
	0.9957	15.4 ±0.1

a. $[Co(NH_3)_5SO_4^+] = 5.5 \times 10^{-4}$ m; Ionic strength = 0.95 m ($LiClO_4$).

TABLE 10. $[H^+]$- and Pressure-Dependences of k_{obs} for $Co(NH_3)_5SO_4^+ + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + SO_4^{2-}$ at 54.99°C.[a]

Pressure (MPa)	$[H^+]$ (mol kg^{-1})	10^5 k_{obs} (s^{-1})
0.1	0.0961	4.48±0.04
	0.1442	4.97±0.02
	0.4807	8.21±0.15
	0.4979	8.38±0.08
	0.9614	13.1 ±0.2
25.0	0.0961	5.35±0.01
	0.1442	5.66±0.02
	0.4807	9.29±0.02
	0.9614	14.1 ±0.1
50.0	0.0961	6.06±0.03
	0.4807	6.58±0.04
	0.4807	10.3 ±0.1
	0.1442	10.4 ±0.1
	0.9614	15.3 ±0.2
75.0	0.0996	6.80±0.03
	0.1494	7.22±0.02
	0.1494	7.26±0.04
	0.4979	11.4 ±0.2
	0.9957	16.8 ±0.2
100.0	0.0996	7.77±0.05
	0.1494	8.17±0.07
	0.4979	12.3 ±0.1
	0.9957	17.8 ±0.2

a. $[Co(NH_3)_5SO_4^+] = 5.5 \times 10^{-4}$ m; Ionic strength = 0.95 m ($LiClO_4$).

Figure 11

Typical plot of k_{obs} vs. $[H^+]$ for aquation of $Co(NH_3)_5SO_4^+$. T = 54.99°C, P = 100.0 MPa.

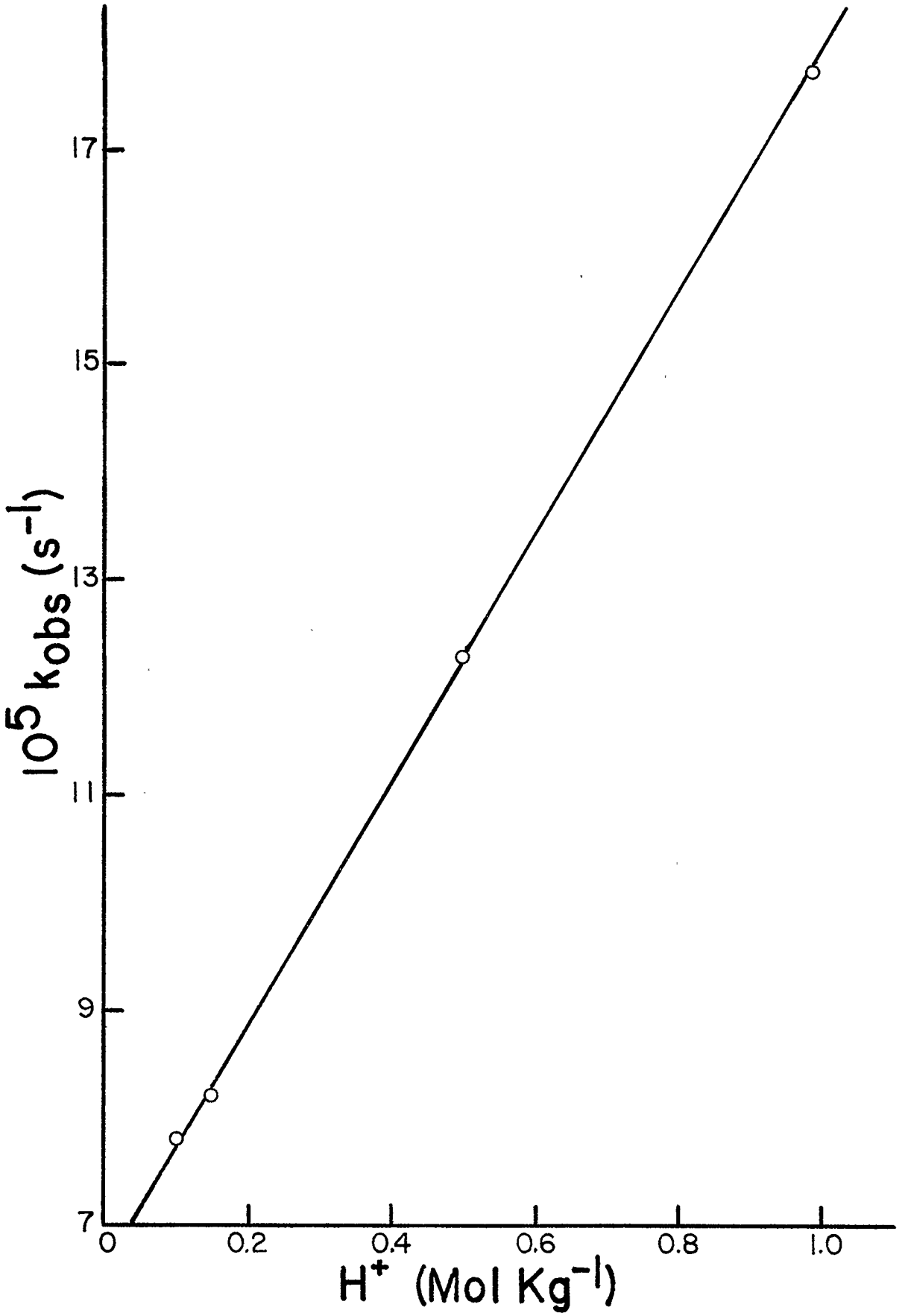

17
15
13
11
9
7
10^5 kobs (s^{-1})
0
0.2
0.4
0.6
0.8
1.0
H^+ (Mol Kg^{-1})

TABLE 11. Pressure-Dependence of Rate Coefficients for Spontaneous and Acid-Catalysed Aquation Pathways of $Co(NH_3)_5SO_4^{+}$[a].

Pressure (MPa)	$10^6\ k_{aq}$ (s^{-1})	$10^6\ k'_H$ (kg $mol^{-1}\ s^{-1}$)
	T = 34.99°C	
0.1	3.39±0.08	6.36±0.17
25.5	4.22±0.11	6.48±0.20
50.5	4.87±0.04	6.70±0.07
75.6	5.55±0.08	7.02±0.13
99.1	6.20±0.07	7.61±0.13
149.6	7.90±0.08	7.59±0.14
	T = 54.99°C	
0.1	35.0±0.5	99.3±0.9
25.0	43.0±0.9	102±2
50.0	50.9±0.9	107±2
75.0	56.3±0.8	113±2
100.0	65.9±0.9	113±2

a. $[Co(NH_3)_5SO_4^{+}] = 5.5 \times 10^{-4}$ m; ionic strength = 0.95 m ($LiClO_4$).

Figure 12

Pressure-dependence of rate coefficients for aquation of $Co(NH_3)_5SO_4^+$. ○ spontaneous □ acid-catalysed T = 34.99°C.

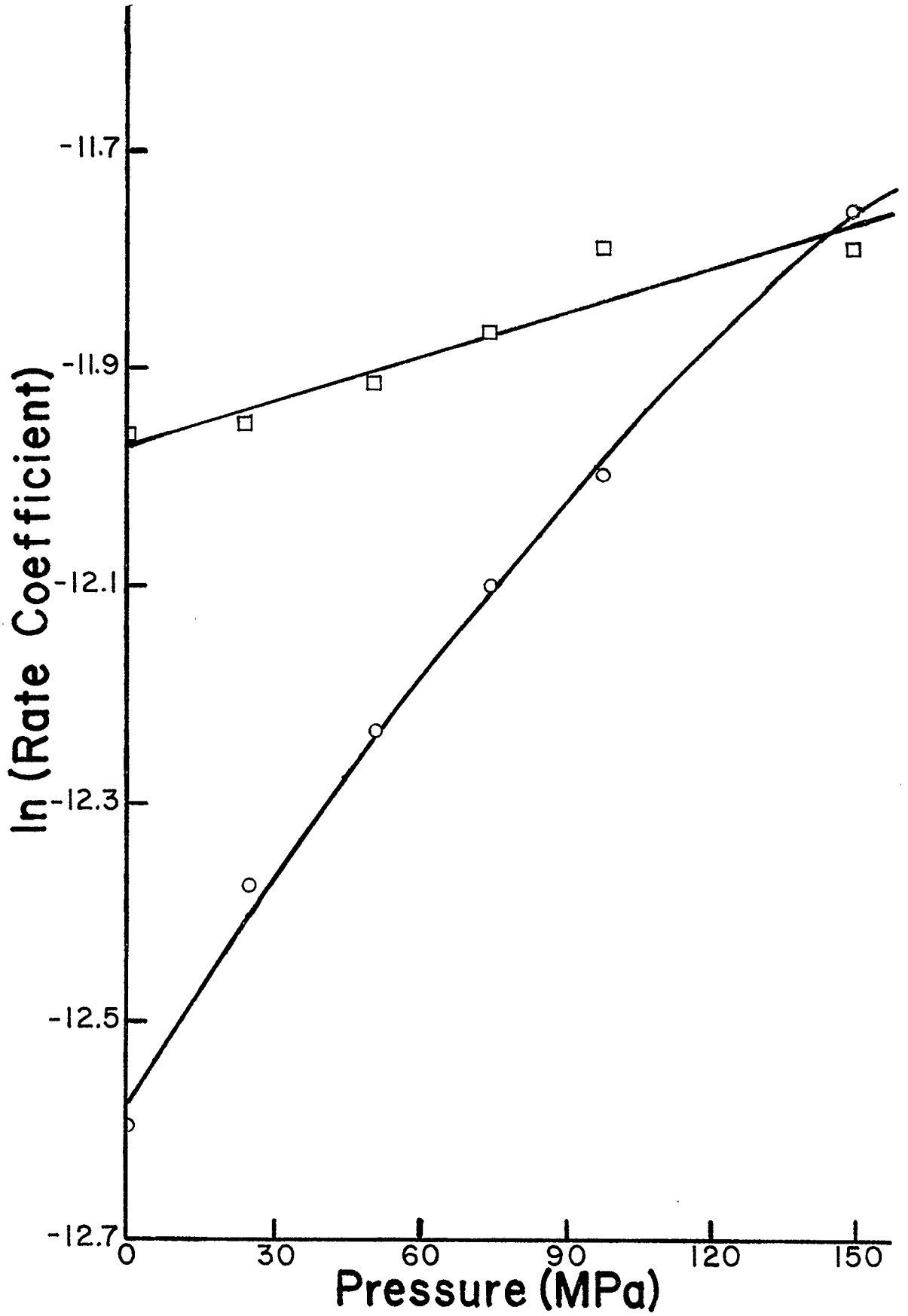
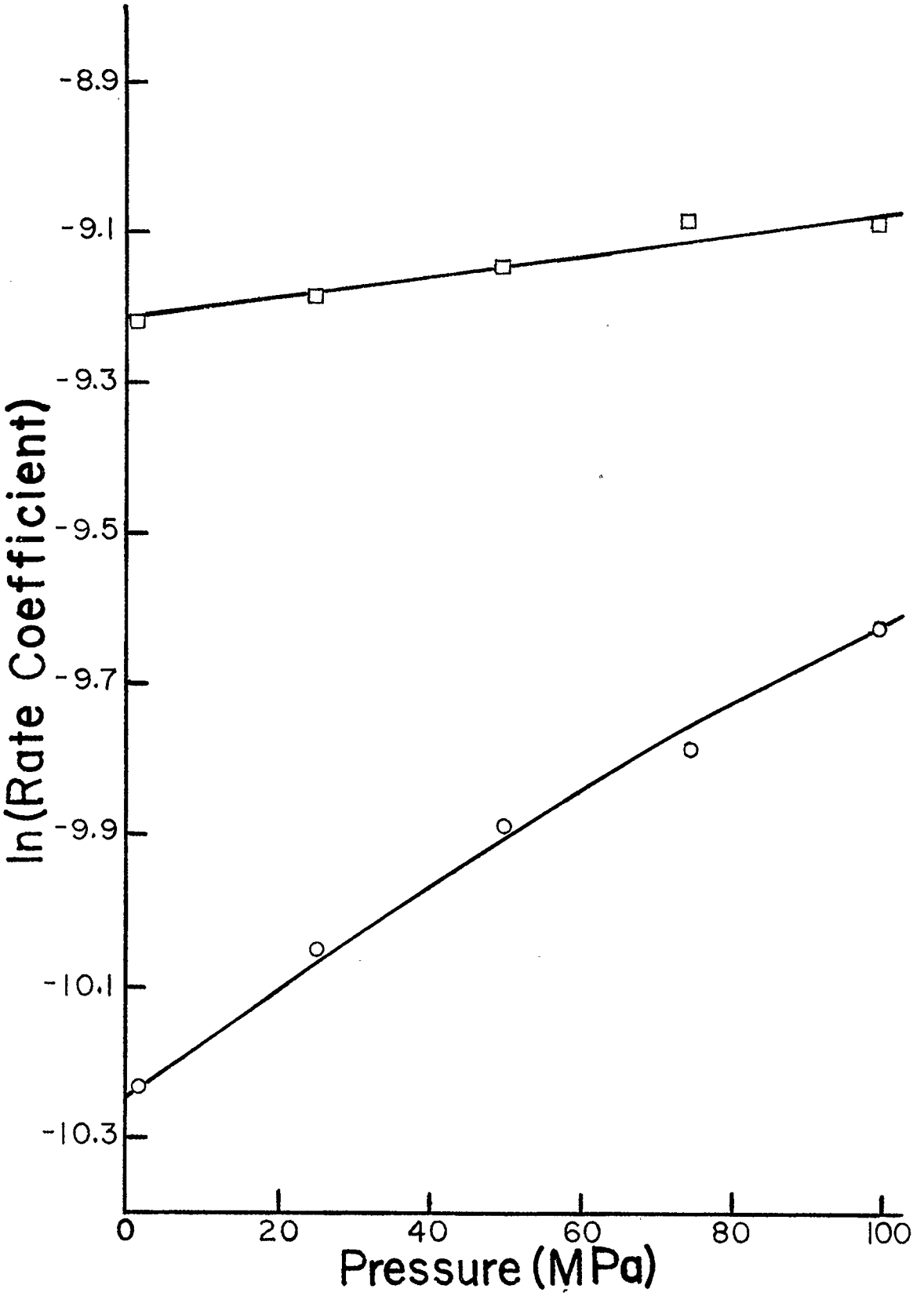

-11.7
-11.9
-12.1
-12.3
-12.5
-12.7
ln (Rate Coefficient)
0
30
60
90
120
150
Pressure (MPa)

Figure 13

Pressure-dependence of rate coefficients for aquation of $Co(NH_3)_5SO_4^+$. ○ spontaneous, □ acid-catalysed. T = 54.99°C.


-8.9
-9.1
-9.3
-9.5
-9.7
-9.9
-10.1
-10.3
ln(Rate Coefficient)
0
20
40
60
80
100
Pressure (MPa)

Densities measured at 35°C were used to calculate ΔV for that temperature using equation 49, where d_o, $d_{CoSO_4^+}$ and $d_{CoOH_2^{3+}}$ are the

$$\Delta V = \frac{1000}{cd_o}(d_{CoSO_4^+} - d_{CoOH_2^{3+}}) \qquad 49$$

densities of the reference, reactant, and product solutions respectively, and c is the molar concentration of the complexes. For [complex] = 8×10^{-3} M and $[H^+] = 7 \times 10^{-4}$ M, $\Delta V = -23.7 \pm 0.7$ cm^3 mol^{-1} at 35°C.

3.2.2 Partial Molal Volumes of Acidopentaammine-cobalt(III) and chromium(III) Species

The apparent molal volumes of the acidopentaamine-cobalt(III) and chromium(III) complexes listed in table 12 were calculated from density data using equation 33 (chapter 3). The partial molal volume of an electrolyte is defined[82] as being the apparent molal volume at infinite dilution. Palmer and Kelm[19] found the apparent molal volumes of these complexes to be constant (within the experimental error) over the concentration range 3.9 - 17.0 $\times 10^{-3}$ M. For this reason, the partial molal volume in each case was taken as being equal to the mean value of the apparent molal volumes obtained. The values of the partial molal volumes obtained in this work are listed in table 12, together with those obtained by Palmer and Kelm[19]. The apparent molal volumes of 0.01 M $HClO_4$ and HCl in water and in 0.98 M $NaClO_4$ were also determined. The values were found to be 45.0 and 46.3 cm^3 mol^{-1} for $HClO_4$ in water and perchlorate solution, respectively and 18.7 and 21.1 cm^3 mol^{-1} for HCl.

4. Discussion

4.1 Volumes of Activation

4.1.1 $[H^+]$-independent Pathway

As shown in figures 12 and 13, the ln k_{aq} vs. pressure plots for

TABLE 12. Partial Molal Volumes of Some Acidopentaammine-cobalt(III) and Chromium(III) Species

Complex	$\overline{V}^{\circ}$ ($cm^3\ mol^{-1}$) this work[a]	$\overline{V}^{\circ}$($cm^3\ mol^{-1}$) from ref. 19
$[Co(NH_3)_6](ClO_4)_3$	207.6	207.1
$[Co(NH_3)_5OH_2](ClO_4)_3$	204.4	206.1
$[Co(NH_3)_5OH_2](ClO_4)_3$	210.6[b]	-----
$[Co(NH_3)_5Cl](ClO_4)_2$	169.4	187.2
$[Co(NH_3)_5Cl](ClO_4)_2$	180.0[b]	-----
$[Cr(NH_3)_5OH_2](NO_3)_3$	171.4	170.4
$[Cr(NH_3)_5OH_2](ClO_4)_3$	215.5	-----
$[Cr(NH_3)_5Cl](ClO_4)_2$	183.4	184.7[c]

a. [Complex] = 1×10^{-2} M.

b. In the Presence of 0.98 M $NaClO_4$.

c. Measurements performed on Monohydrate. $\overline{V}^{\circ}$ has been corrected accordingly.

the uncatalysed aquation pathway show slight but unmistakable curvature even over the limited pressure range studied here. Thus no attempt was made to fit the data to the linear function (equation 12). Instead, the quadratic (equation 36) and modified Tait (equation 38) expressions were used. The latter expression was applied twice, once using the value of x found by Jones et. al.[66] (x = 8.0), and once leaving x as a variable. None of the equations gave a significantly better fit of the data at either temperature than did the others. The coefficients of correlation were all within ±0.0007 of 0.9972 at 35.0°C and within ±0.0005 of 0.9953 at 55.0°C. In view of the fact that Jones' data were gathered over a much wider range of pressures than was used in the present work, his data should give a more precise estimate of the curvature (but not of ΔV_0^*) to be expected in this system. Thus the ΔV_0^* values derived from the Tait expression assuming x = 8.0 will be taken as being the "best" values. Thus the values of ΔV_0^* are found to be -18.3±0.4 $cm^3\ mol^{-1}$ at 35.0°C and -19.7±0.8 $cm^3\ mol^{-1}$ at 55.0°C.

4.1.2 $[H^+]$-catalysed Pathway

The data for this pathway were insufficiently precise to warrant application of any function other than the linear one. The values of ΔV^* obtained from a linear least squares treatment were -3.5±0.6 $cm^3\ mol^{-1}$ at 35.0°C and -3.9±0.5 $cm^3\ mol^{-1}$ at 55.0°C.

Kendall and co-workers[103] have suggested a ΔV for the rapid protonation step in an acid-catalysed aquation of about 2 $cm^3\ mol^{-1}$, based upon studies of reactions of the type shown in equation 50. A similar

$$M(OH_2)_5(OH)^{(n-1)+} + H^+ \rightleftharpoons M(OH_2)_6^{n+} \qquad 50$$

volume change would be expected for the protonation of $Co(NH_3)_5SO_4^+$

(equation 44). Since the overall ΔV^* for the acid-catalysed aquation (equations 44 and 45) is -3.7 $cm^3\ mol^{-1}$, then ΔV^* for the rate-determining step (equation 45) must be about -5.7 $cm^3\ mol^{-1}$. Thus ΔV^* for the rate-determining step of the acid-catalysed pathway is approximately 13.3 $cm^3\ mol^{-1}$ more positive than that for the spontaneous aquation pathway.

Klotz and Eckert[104] found the ΔV for acid dissociation of the HSO_4^- ion to be -20.2 $cm^3\ mol^{-1}$ at 25°C. Combining this value with the partial molal volume of the proton (-5.4 $cm^3\ mol^{-1}$)[82], it is found that $\overline{V}^\circ_{HSO_4^-}$ is 14.8 $cm^3\ mol^{-1}$ more positive than $\overline{V}^\circ_{SO_4^{2-}}$. Assuming that the temperature-dependences of $\overline{V}^\circ_{HSO_4^-}$ and $\overline{V}^\circ_{SO_4^{2-}}$ are similar, so that the difference between them does not change significantly over a 30° temperature range, it would appear that the difference between the ΔV^* values of the catalysed and uncatalysed aquation pathways can be accounted for solely on the basis of the difference in partial molal volumes of their respective leaving groups. Thus the acid-catalysed aquation seems to occur via an I_d pathway very similar to that by which the spontaneous aquation proceeds. A similar conclusion was reached by Monacelli[50] on other grounds.

4.1.3 The Effect of Temperature on ΔV_0^*

The effect of temperature on the value of ΔV_0^* has been investigated for the Menschutkin reaction between triethylamine and ethyl iodide[105,106] and for the hydrolysis reactions of several alkyl halides[107]. In all cases negative ΔV^* values were involved, and for all but two of the alkyl halide hydrolyses, the ΔV^* values were found to become more negative with increasing temperature. The larger volume changes at higher temperatures were attributed to thermal expansion of the solvent. In

these reactions the transition state is more highly solvated than the reactants. The change in volume experienced by the solvent on going from the bulk region to the solvation sheath of the transition state is greater at higher temperatures where the molar volume of the bulk solvent is larger. The failure of two of the alkyl halide hydrolyses to conform to this pattern was attributed to reduced accessibility of solvent to the developing carbonium ion centres.

Merbach et. al.[28] studied the solvent exchange of $Co(DMF)_6^{2+}$ in DMF at -20°C and +23°C using high pressure N.M.R. techniques. Within the experimental error suggested by the authors (± 1-2 cm^3 mol^{-1}) the ΔV^* value for this system is independent of temperature over the range studied. This was to be expected for a reaction in which the solvational contribution to ΔV^* is near zero.

For both the uncatalysed and catalysed aquations of $Co(NH_3)_5SO_4^+$ the effect on ΔV_0^* of changing the temperature by 20°C is small. Indeed for the acid-catalysed path, the variation with temperature is significantly less than the experimental error, and can thus be neglected. For the uncatalysed pathway the change in ΔV^* with temperature is only slightly greater than the experimental error, and hence a failure to consider temperature differences in a comparison of ΔV^* values from different sources would not introduce a serious error.

In quantitative terms, ΔV_0^* for acid-independent aquation of $Co(NH_3)_5SO_4^+$ is 1.4 cm^3 mol^{-1} more negative at 55.0°C than at 35.0°C. The temperature-dependence of ΔV_0^* would be expected to reside in the solvational component, as was the case for the organic systems mentioned above. The Tait equation indicates that the transition state is solvated by 8.0 more molecules of water than is the initial state. The molar volume of water in the bulk solvent is 18.12 cm^3 mol^{-1} at 35.0°C and

18.28 cm^3 mol^{-1} at 55.0°C[108]. Using these values, the change in ΔV_s^* to be expected on going from 35.0°C to 55.0°C would be 8.0 (18.12) - 8.0 (18.28) = -1.3 cm^3 mol^{-1}, which is in excellent agreement with the observed change in ΔV_0^*. Hence, as predicted, changes in the solvational contribution to ΔV_0^* with temperature account for all of the change in the overall value of ΔV_0^*.

Since most complex ion reactions in water involve a smaller degree of solvational change on going to the transition state than does the spontaneous aquation of $Co(NH_3)_5SO_4^+$, the effect of temperature on ΔV_0^* will generally be even less significant than it is in this system. In nonaqueous solvents such as DMF and DMSO thermal expansion would result in larger volume changes with increasing temperature due to the larger molar volumes of these solvents relative to water. The results obtained here suggest that the change in ΔV_0^* to be expected could be estimated easily if x from the Tait equation were known at one temperature.

4.1.4 Comparison of the ΔV^* Values from Different Sources

The values of ΔV^* obtained for the uncatalysed aquation of $Co(NH_3)_5SO_4^+$ by Jones et. al.[66], van Eldik and co-workers[55], and in this work are summarised in table 13.

The results obtained in this work are in excellent agreement with that from reference 66, in spite of the difference in ionic strength. Moderate changes in ionic strength would not be expected to cause much variation in the ΔV^* value for an aquation reaction, since ion-pairing occurs only after the transition state has been passed.

The values of ΔV_0^* reported by van Eldik et. al.[55] do not agree at all well with those obtained by other workers. Failure of their data to correlate with that of Jones[66] had been attributed to the temperature

TABLE 13. Values of ΔV^* for the Uncatalysed Aquation of $Co(NH_3)_5SO_4^+$ Under Various Conditions

Temperature (°C)	ionic strength (mol L^{-1})	$[H^+]$ (mol L^{-1})	ΔV_0^* (cm^3 mol^{-1})	Reference
25	0.1	5×10^{-5}	-18.5±0.7	66
35	1.0	0	-18.3±0.4	This Work
55	1.0	0	-19.7±0.8	This Work
60	2.0	0.1	-8.2±1.2	55
60	0.1	0.1	-8.1±0.6	55
60	0.1	3×10^{-5}	-8.0±0.4	55

difference between the two studies. The results of the present study have shown this explanation to be untenable. Two other factors taken together can account for this discrepancy.

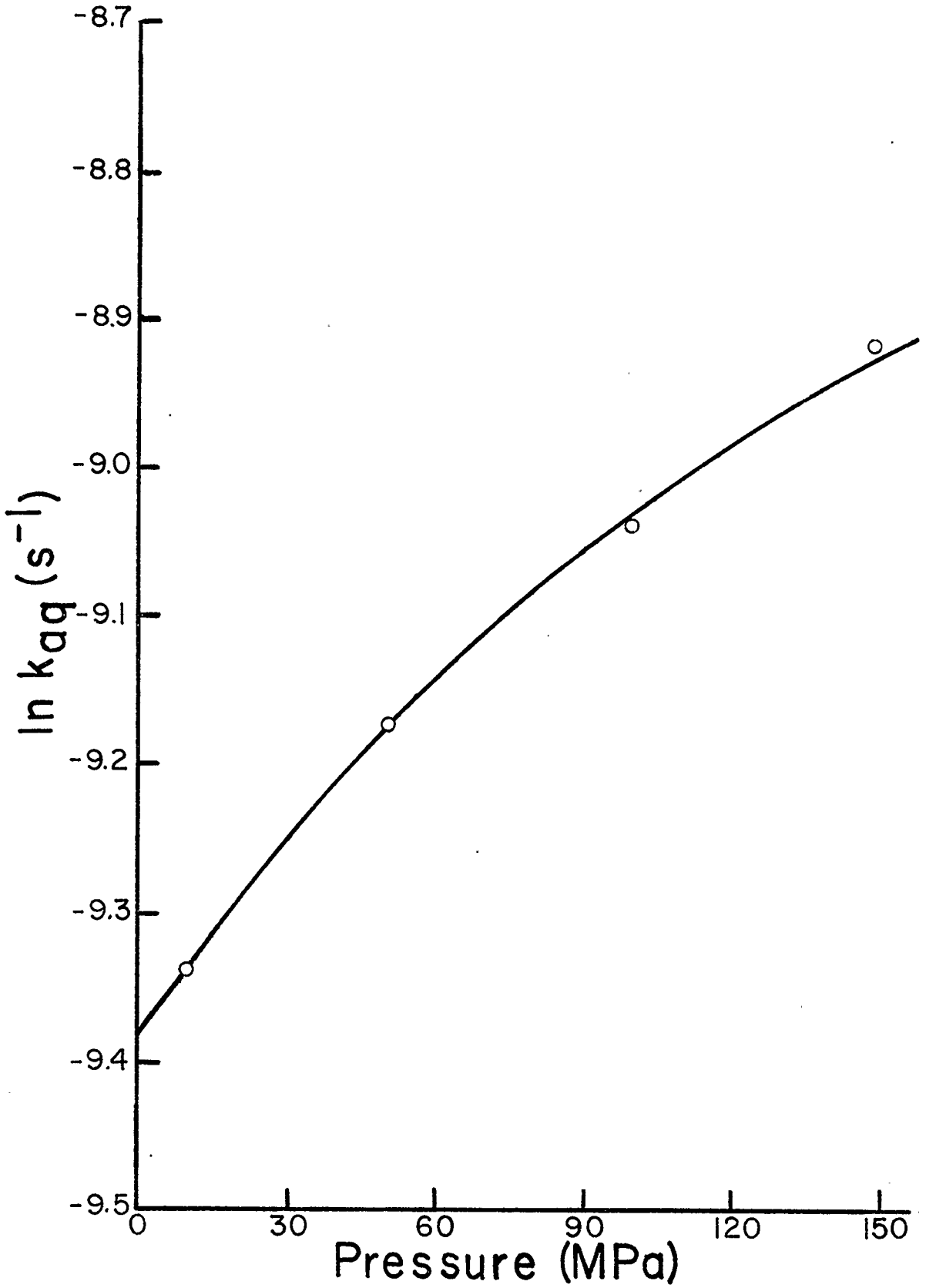
Firstly, van Eldik et. al.[55] have indicated that the ΔV_0^* values for aquation at 0.1 M $[H^+]$ and 3×10^{-5} M $[H^+]$ are the same. This can be true only if the acid-catalysed pathway does not make a significant contribution to the overall reaction rate in 0.1 M acid, or if the ΔV_0^* values for the acid-catalysed and uncatalysed pathways are equal. That the aquation of $Co(NH_3)_5SO_4^+$ is $[H^+]$-dependent to a significant extent was noted by Taube and Posey[94] in 1953. Monacelli[50] studied the acid-catalysed pathway in detail at 0.1 MPa. The present work shows that the acid-catalysed pathway accounts for 20-25% of the reaction rate at 55.0°C, 0.1 MPa and 0.1 M $[H^+]$. Furthermore, ΔV_0^* for the acid-catalysed pathway is much less negative than that for the uncatalysed path. Using the data obtained in this work, it is found that ΔV_0^* for the overall aquation process is 2 to 3.5 $cm^3\ mol^{-1}$ less negative at 0.1 M $[H^+]$ than at zero acidity.

Secondly, the authors of reference 55 have fitted their high pressure rate data to a linear function. Figure 14 shows a plot of the data from reference 55. The plot is clearly not linear. Application of the Tait equation to this data (assuming x = 8.0) yields a value of ΔV_0^* of $-12.6 \pm 1.7\ cm^3\ mol^{-1}$.

If the ΔV_0^* of reference 55 is corrected for both the acidity difference and the non-linearity of the ln k vs. pressure plot, a value of approximately $-16\ cm^3\ mol^{-1}$ is obtained. The value is now in reasonably good agreement with that of other workers.

Figure 14

Plot of ln k_{aq} vs. pressure
using data from reference 55.


-8.7
-8.8
-8.9
-9.0
-9.1
-9.2
-9.3
-9.4
-9.5
ln kaq (s⁻¹)
0
30
60
90
120
150
Pressure (MPa)

4.1.5 ΔV for Acid-Independent Aquation of $Co(NH_3)_5SO_4^+$

The value obtained for ΔV at 35.0°C and 0.08 m ionic strength is in reasonable agreement with that obtained by Spiro and co-workers[25] at 30.0°C and $\sim$ 0.05 m ionic strength, the two values being -23.7 and -19.2 $cm^3\ mol^{-1}$, respectively. Spiro's results show that ΔV becomes $\sim$ 4 $cm^3\ mol^{-1}$ less negative when the ionic strength is increased to $\sim$ 0.95 m. Thus in the present work a ΔV of -19.7 $cm^3\ mol^{-1}$ would be expected at 35.0°C and the ionic strength of the kinetic experiments. The ΔV value is 1.4 $cm^3\ mol^{-1}$ more negative than the ΔV_0^* obtained under the same conditions. This confirms the results of Jones et. al.[66] which indicated that the transition state in an I_d mechanism closely resembles the products.

4.2 The Partial Molal Volumes of Pentaammine-cobalt(III) and chromium(III) Species in Water

The two sets of data given in table 12 are in good agreement with one another with the exception of the results given for $[Co(NH_3)_5Cl](ClO_4)_2$. The value obtained for this complex in the present work is 17.8 $cm^3\ mol^{-1}$ smaller than that reported by Palmer and Kelm[19]. The difference is almost exactly equal to the molar volume of water (18.0) and would account for the fact that Palmer and Kelm found it necessary to assume a $\overline{V}^\circ_{H_2O}$ value of zero when calculating ΔV for the aquation of the complex.

There is reason to believe that the discrepancy between the two values may have arisen from differences in the preparative procedures used. It was found in this work that the use of a sample of $[Co(NH_3)_5Cl](ClO_4)_2$ recrystallised from concentrated $HClO_4$ gave a $\overline{V}^\circ$ of 179.2 $cm^3\ mol^{-1}$ in contrast to the value of 169.4 $cm^3\ mol^{-1}$ obtained using a

sample recrystallised from dilute $HClO_4$. The use of concentrated $HClO_4$ in recrystallisations of acidopentaamminecobalt(III) perchlorate complexes is not uncommon, since aquation of these complexes occurs quite rapidly if they are not quickly reprecipitated. Use of concentrated $HClO_4$ greatly increases the risk of having $HClO_4$ adsorbed onto the surface of the final product. Such contamination might not be evident from the results of an equivalent weight determination or a total halogen content analysis, since any loss of H^+ or halide resulting from the reduced number of moles of complex in a given weight of substance might be compensated for by the H^+ or Cl in the adsorbed acid.

The ΔV for the aquation of $Co(NH_3)_5Cl^{2+}$ can be calculated using equation 47. The values of $\overline{V}^{\circ}_{ClO_4^-}$ and $\overline{V}^{\circ}_{Cl^-}$ quoted in reference 19 allow calculation of the ionic partial molal volumes of the complexes. Using the $\overline{V}^{\circ}_{H_2O}$ for 25°C (18.0 cm^3 mol^{-1}), ΔV is found to be -12.0 if the value for the chloro-complex determined in this work is used and -29.8 if the value from reference 19 is used. The directly determined value of ΔV is -11.6 cm^3 mol^{-1} [66] at 0.1 M ionic strength.

Data are also given in this work which allow calculation of ΔV for the aquation of $Co(NH_3)_5Cl^{2+}$ in 0.98 M $NaClO_4$. The value obtained is -12.6 cm^3 mol^{-1}. This agrees quite well with the experimental value found by Spiro et. al.[25] which is -10.4 cm^3 mol^{-1}.

The question remains as to whether Palmer and Kelm's partial molal volumes for the other acidopentaamminecobalt complexes used are also $\sim$ 18 cm^3 mol^{-1} too high. A sample of $[Co(NH_3)_5Br](ClO_4)_2$ recrystallised from concentrated $HClO_4$ was found to give a $\overline{V}^{\circ}$ of 184.1 cm^3 mol^{-1}, compared to 196.4 cm^3 mol^{-1} quoted in reference 19. This does suggest that the value obtained for the partial molal volume of this complex is also

sensitive to the method of preparation. A further reduction in $\overline{V}^{\circ}$ might be observed for a sample recrystallised from dilute $HClO_4$. No other experimental data are currently available for the acidcpentaammine-cobalt(III) complexes.

Another reason for suggesting that the observed $\overline{V}^{\circ}$ values for the cobalt complexes might be too high is the unreasonableness of assuming that $\overline{V}^{\circ}_{H_2O} = 0$ in reactions of these complexes. Even coordinated water, which may be regarded as being under 10^3 MPa of pressure[4b] and thus highly compressed, has an estimated $\overline{V}^{\circ}$ of ~ 14 cm^3 mol^{-1} [109].

The values of $\overline{V}^{\circ}_{Co(NH_3)_5{}^{3+}}$ calculated from the data for the aquo- and chloropentaamminecobalt(III) complexes obtained in this work using $\overline{V}^{\circ}_{H_2O} = 18.0$ cm^3 mol^{-1} are 35.5 and 35.65 cm^3 mol^{-1}, respectively. The similarity of these two numbers suggests that Palmer and Kelm's volume profile method[19] may indeed allow a distinction to be made between I_a and I_d mechanisms if reliable $\overline{V}^{\circ}_{complex}$ values can be obtained. Their suggestion that $Co(NH_3)_6{}^{3+}$ might be a good model for the $Co(NH_3)_5{}^{3+}$ transition state species, however, is not borne out by these results, since $\overline{V}^{\circ}_{Co(NH_3)_6{}^{3+}}$ is ~ 20 cm^3 mol^{-1} larger than the corresponding value for the $Co(NH_3)_5{}^{3+}$ species. This difference is only slightly less than the molar volume of aqueous NH_3 (25 cm^3 mol^{-1}; calculated from data in references 82, 90 and 110). As mentioned in chapter one, the assumption that an intermediate of reduced (or increased) coordination number has the same volume as its parent complex neglects the effect of changes in bond-lengths to the non-labile ligands. In the present context, it also neglects the possibility that $Co(NH_3)_5{}^{3+}$ and $Co(NH_3)_6{}^{3+}$ are slightly differently solvated.

5. Conclusions

The volumes of activation for the spontaneous and acid-catalysed aquation pathways of $Co(NH_3)_5SO_4^+$ were found to differ only by the amount of the difference in volume of their respective leaving groups. This suggests that the rate-determining step of the acid-catalysed path proceeds by an I_d mechanism analogous to that occurring for the spontaneous aquation.

The results at 35° and 55°C indicated that ΔV_0^* is only slightly temperature-dependent in aqueous systems. The slight dependence was found to reside solely in the solvational component of ΔV_0^*, and could be quantitatively accounted for by consideration of the thermal expansivity of the water molecules gained on going to the transition state.

Density measurements on several ligandopentaammine-cobalt(III) and chromium(III) complexes suggested that the $\overline{V}^\circ$ values obtained by Palmer and Kelm[19] for some of the cobalt complexes were too high, apparently because of the presence of adsorbed $HClO_4$ on the surface of the solid complexes. The results obtained in the present work vindicate the volume profile approach for distinguishing between I_a and I_d mechanisms, but suggest that $Co(NH_3)_6^{3+}$ is not a good model for the $Co(NH_3)_5^{3+}$ transition state species.

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