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ACTIVATION VOLUMES OF THE REACTIONS OF TRANSITION METAL COMPOUNDS IN SOLUTION

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A. GENERAL ASPECTS OF HIGH PRESSURE KINETICS

(i) Introduction

The history of high pressure kinetic studies in organic chemistry extends over a period of more than 80 years. During this time the volume of activation, $\Delta V^{\neq}$, has become an accepted mechanistic criterion and this topic has been reviewed on numerous occasions [1—15]. In contrast, the first high pressure inorganic study was reported as recently as 1955 [16] and only two detailed reviews exist [17,18] devoted solely to inorganic reactions, apart from a recent short survey [19] and a review of the general field of "High Pressure in Coordination Chemistry" in 1974 [20]. Consequently many inorganic chemists remain unaware of the implications and applications of this technique.

The fact that the majority of coordination compounds are charged often introduces a complicating factor into the interpretation of $\Delta V^{\neq}$. However this problem also arises in the rationalization of the more widely used activation parameters, viz. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ [21]. The concept of a volume change can be at least more readily visualized than the more intangible entropy of activation. More importantly, the generally superior accuracy of $\Delta V^{\neq}$, coupled with the possibility of measuring both the overall volume change, $\Delta \overline{V}$, and the absolute volume of the proposed transition state make this parameter a very strong mechanistic tool.

(ii) Theory

The units of pressure most commonly used are the bar and the normal atmosphere (atm). However, other units, such as the pascal (Pa), Newton per square meter (N m^{-2}) and pounds per square inch (p.s.i.) have also been adopted. The relationships between these units are as follows:

$$
\begin{aligned}
1 \text{ bar} &= 1 \text{ dyne cm}^{-2} = 10^5 \text{ Pa} = 10^5 \text{ N m}^{-2} \\
&= 0.986923 \text{ atm} = 1.019716 \text{ kg cm}^{-2} \text{ (at)} \\
&= 14.504 \text{ p.s.i.}
\end{aligned}
$$

Within the framework of the transition state theory [22,23], the volume of activation is derived from the pressure dependence of the rate constant, k_{obs}, of a reaction

$$(\partial \ln k/\partial P)_T = -\Delta V^{\neq}/RT + \Delta\nu\kappa RT \qquad (1)$$

The second term on the right hand side of the equation only applies when k is expressed in pressure dependent units, i.e. molarity. This correction term consists of $\Delta\nu$ which is the sum of stoichiometric indices of the transition state and reactants (the indices on the left hand side of the reaction equation are conventionally given a negative sign) and κ, which represents the compressibility coefficient of the reaction medium. In aqueous solution, for example, the correction term amounts to 1.1 $cm^3\ mol^{-1}$ at 25°C and 1 bar for a second-order associative process and 2 to 4 $cm^3\ mol^{-1}$ for most organic solvents.

If the pressure range is sufficiently extended in any given system, $\Delta V^{\neq}$ becomes pressure dependent. Thermodynamically this is analogous to the second temperature derivative of the free energy of activation. The compressibility coefficient of activation, $\Delta\beta^{\neq}$, is therefore defined as

$$\Delta\beta^{\neq} = -(\partial \Delta V^{\neq}/\partial P)_T \tag{2}$$

From this quantity the compressibility of activation, $\Delta\kappa^{\neq}$, can be derived

$$\Delta\kappa^{\neq} = \Delta\beta^{\neq}/\Delta V^{\neq} \tag{3}$$

Both parameters involve the difference in compressibility between the transition state and the reactants. As is the case for $\Delta C_p^{\neq}$, it is experimentally difficult to obtain accurate values for these two quantities. Furthermore, their exact significance is somewhat controversial. Despite these shortcomings, $\Delta\beta^{\neq}$ has been used successfully in a number of cases to characterize reaction mechanisms.

The activation parameters mentioned up to this point are derived on the basis of the transition state theory. However, the applicability of this theory to reactions in solution has occasionally been criticized [24,25]. If the transition state theory is valid for such reactions, then the Maxwell Relations must also apply to the various activation parameters, e.g. $-(\partial \Delta V^{\neq}/\partial T)_P = (\partial \Delta S^{\neq}/\partial P)_T$. Although precise kinetic data are needed to rigorously establish the validity of these equations, at least five systems have been investigated (three inorganic [26—28], two organic [29,30] and a thermally-activated photophysical process [31]) for which the Maxwell equations hold. It is more convenient to rearrange the Maxwell equation into the form, $(\partial \Delta H^{\neq}/\partial P)_T = \Delta V^{\neq} - T(\partial \Delta V^{\neq}/\partial T)_P$, for this purpose. The results of the cited example [27] (i.e. the substitution reaction of $Pt(dien)Cl^+$ with azide ion in water) are presented in Table 1.

TABLE 1

Application of the Maxwell relationship to the activation parameters of the substitution reaction of $Pt(dien)Cl^+$ with N_3^- in aqueous solution [27]

T (K)	$\Delta V^{\neq}$ ($cm^3\ mol^{-1}$)	$(\partial \Delta H^{\neq}/\partial P)_T$ ($J\ mol^{-1}\ bar^{-1}$)	$\Delta V^{\neq} - T(\partial \Delta V^{\neq}/\partial T)_P$ ($J\ mol^{-1}\ bar^{-1}$)
298	−8.2	8.6	8.5
308	−11.7	8.6	8.5
318	−14.4	8.6	8.5

(iii) Treatment of high pressure kinetic data

As mentioned earlier, $\Delta V^{\neq}$ is generally dependent on pressure. As the volume of activation at ambient pressure, often symbolized by $\Delta V_0^{\neq}$, is of primary interest to the chemist, the problem of finding a suitable equation to fit the (ln k) pressure data has been treated by various researchers [32—34]. The quadratic equation is probably the most commonly adopted expression,

$$\ln k = A + BP + CP^2 \qquad (4)$$

whereby $\Delta V_0^{\neq} = -BRT$ and $\Delta\beta_0^{\neq} = 2\,CRT$. This method is adequate as long as $\Delta V^{\neq}$ does not vary too acutely with pressure. Lohmüller et al. [33] investigated the pressure dependence of the solvolysis rate of benzyl chloride and concluded that the parabolic expression fits the data better than other equations. However there is no physical justification for using this function or the corresponding fraction form

$$\ln k = A + BP/(C + P) \qquad (5)$$

whereby $\Delta V_0^{\neq} = -BRT/C$ and $\Delta\beta_0^{\neq} = -2B/C^2$. At pressures greater than 100 C the function becomes essentially independent of pressure (i.e. $\Delta V^{\neq} = 0$) which is not consistent with the inherent concept of $\Delta V^{\neq}$. Nevertheless, at moderate pressures the fractional function is a useful method for treating experimental data. A similar equation was proposed to describe the pressure dependence of dissociation constants of weak acids [35].

A further variation exists in the form of the exponential function,

$$\ln k = A + B(1 + \exp(-CP)) \qquad (6)$$

This seldom-used expression has the same limitations as eqn. (5).

The functions based on the Tait equation, which is an empirical equation for the compressibility of organic solvents, bear at least some resemblence to the real situation involved in volume changes. Benson and Berson [32] used this approach to formulate

$$(1/P)\ln(k_P/k_0) = A + BP^{0.523} \qquad (7)$$

The exponent 0.523 is valid only in the pressure range 2 to 10 kbar and for organic solvents. The extrapolation to $P = 0$ ($\Delta V_0^{\neq} = -ART$) is long and a source of error. Equation (7) is therefore not suitable when the curvature is acute at low pressures ($\Delta\beta_0^{\neq}$ is equal to 0.797 BRT). Hamann [1] has criticized Benson and Berson's use of the Tait equation which predicts negative volumes of activation at very high pressures, e.g. $>4 \times 10^3$ kbar. More recently, another equation based on the modified Tait equation was proposed by Swaddle and co-workers [36] for reactions in aqueous solution

$$\ln k = \ln k_0 - P\,\Delta V_0^{\neq}/RT - (30.17x/T)\{(P + 3.06)\ln(1 + P/3.06) - P\} \qquad (8)$$

where x is the increase in the number of water molecules solvating the complex as it goes to the transition state. This was designed to account for the compressibility of water in an idealized model for the solvation of inorganic complex ions. The authors [36] demonstrated that eqn. (8) was an improvement over the more conventional quadratic function for their system.

In an attempt to avoid imposing an empirical expression on the data, a graphical technique has been used by Baliga and Whalley [37]. This is called the incremental method and exists in two similar forms [34]. The generalized form is

$$\ln\{k_{(p_i+1)}/k_{(p_i)}\}/(p_{i+1} - p_i) = A + B\{(p_{i+1} + p_i)/2\} \tag{9}$$

where $\Delta V_0^{\ddagger} = -ART$ and $\Delta\beta_0^{\ddagger} = 2\,BRT$. As pointed out previously [33], this method is mathematically equivalent to the reduced quadratic equation.

Although the quadratic equation is generally favored by organic chemists [3,7,10,33] it would appear that each system must be evaluated separately to find the most satisfactory fit.

It is of interest to note that at sufficiently high pressures, assuming the system remains in the liquid state, the observed volumes of activation for bimolecular reactions will eventually become positive. At this point the velocity of the reaction becomes limited by the rate of diffusion of the reactants due to the increased viscosity of the medium. The effect was first reported by Hamann [38] for the alkaline etherification of ethyl bromide, where in isopropanol the reaction rate reached a maximum at ca. 35 kbar. Naturally this phenomenon is not encountered at the relatively low pressures of <5 kbar applied to most inorganic reactions, especially for those in aqueous solution. Consequently, the appearance of either a maximum or minimum in the (ln k) versus pressure plots is indicative of a secondary reaction (it may take the form of a parallel pathway, a consecutive reaction, or may even be due to a reaction involving impurities in the system) with a volume of activation of opposite sign to that of the "primary" reaction.

(iv) High pressure equipment

One reason for the increased interest in high pressure chemistry over the last decade can be traced to the recent technical advances in high pressure equipment which have led to its greater versatility. The majority of valves, pumps, manometers, pressure intensifiers, autoclaves, tubing and joints are commercially available. An optical cell capable of withstanding almost 7 kbar can also be purchased. The general scheme of a high pressure apparatus is shown in Fig. 1. Pressures of 3 kbar can be easily attained with a manual hydraulic pump without the aid of a pressure intensifier. For certain measurements, such as in situ spectrometry, it is desirable to have a "transparent" liquid in the pressure vessel. This can be accomplished by inserting a separation column into the system. Water or higher alkanes (e.g. heptane) are frequently used as the transmission fluid, while various high pressure oils are used in the pump-manometer branch of the system. The separation chamber usually contains either a flexible teflon tube as a separating membrane or a float-

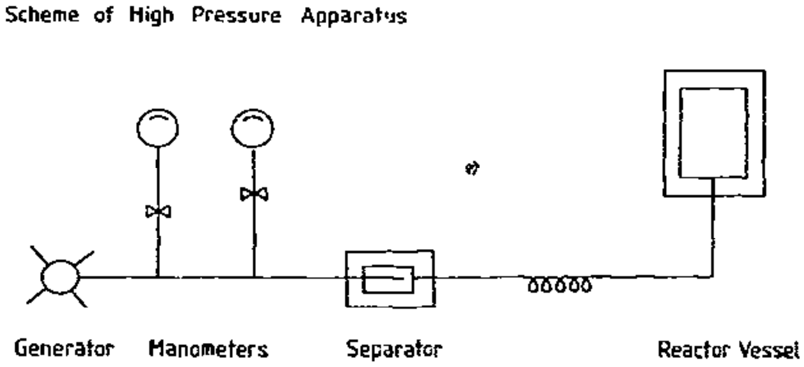


Fig. 1. Diagram of high pressure apparatus.

ing, spring-loaded piston. Compressed inert gas, for example, may also be used to pressurize the reaction solution, thereby eliminating the need for a separation membrane, but at the same time increasing the potential hazard of the system [39].

The most versatile analytical technique in high pressure kinetics involves taking aliquots from a pressurized reaction solution at specific time intervals. The pressure vessel used for this purpose has been described in detail by Whalley [2] and Osborn and Whalley [40]. The solution is contained in either a modified syringe or bellows arrangement suspended in oil within the vessel which is sealed by a screw plug with the lined capillary through its center for removing the samples by way of a fine dosage valve. The plug is generally fitted with a Bridgman unsupported-area seal [3,41]. This technique requires large reaction volumes and is best suited to slower reactions because a considerable amount of time is lost initially during the loading of the vessel, pressurization and subsequent thermal equilibration. However, a smaller version of this assembly has been devised [42] from which micro samples can be withdrawn and has the advantage of mixing two pressurized, thermally-equilibrated solutions to initiate the reaction.

The most commonly used method for monitoring inorganic reactions is in situ spectrophotometry. A variety of modified glass and quartz cells have been developed for this purpose [7,39,43—47]. Inexpensive sapphire discs serve as windows in the pressure vessel, although for certain specific applications, such as for optical rotation measurements [48], quartz discs must be utilized. Spectrophotometric cells have also been designed [49] to enable solutions to be mixed under pressure, similar to the micro sampling device mentioned above [42], thereby making it possible to investigate reactions with half-lives of the order of 10 to 20 s.

Conductivity provides a further means of following chemical processes where a change in the overall charge of the system is involved. Insulated electrical leads can be fed through the walls of the pressure vessel without difficulty [50,51]. Here again, a number of different cell designs have been employed [52—54], although those which require mercury as the pressure transmitting medium are generally unsuitable for inorganic reactions. Moreover, platinum wire-glass seals are fragile and often tend to break under pressure. Therefore cells made of teflon or similar polymeric materials (eg. KELF and VESPEL) are advantageous despite the fact that their cell constants are pressure sensitive, as this does not affect kinetic measurements conducted under first- or pseudo-first-order conditions.

More rapid reactions may be followed spectrophotometrically using the type of pressurized stopped-flow apparatus developed by Heremans [55]. The entire unit (drive and stop syringes, mixing and observation chamber, as well as a stepwise drive motor) is placed inside a pressure vessel. The deadtime of this instrument was reported to be ca. 40 ms. A high pressure stopped-flow apparatus based on a different concept was recently described [56]. This version is capable of withstanding 1.5 kbar and has a dead time of 3 s. The two drive syringes and measuring cell are contained in individual high pressure vessels and mixing is accomplished by allowing the pressurized solutions to flow into an evacuated length of pressure tubing. This operation involves a pressure drop of ca. 40 bar.

Relaxation techniques, such as T-jump and NMR, have also been adapted for use at high pressures. The temperature jump is instigated either by discharging a condenser across two platinum electrodes in the reaction cell [57] or by a laser pulse directed at right angles to the observation axis of the cell [58]. High pressure NMR has made significant gains over the last five years during which time the original rotating quartz tubes [59] have been more or less superseded by probes of certain polyamide plastics [60]. Furthermore, static high pressure systems have been created using various metal alloy probes [60,61]. This method introduced a noticeable improvement in resolution [60].

This summary of the techniques available to the inorganic kineticist is by no means complete (e.g. a pressure jump technique has also been perfected [62]), but is at least representative of the methods commonly used in solution kinetics. Certainly high pressure IR/Raman studies [63] are of the utmost importance in solid state work where much higher pressures are applied.

The overall volume change of a reaction is usually measured with a dilatometer and basically involves determining the height of the reaction solution in a capillary tube, seated atop a calibrated flask, before and after reaction [64,65]. The flask may also be constructed with two chambers to separate the potential reaction solutions with the result that $\Delta \overline{V}$ for rapid reactions can be measured, e.g. acid—base neutralizations [66,67]. By placing a uniform, calibrated resistance wire in the capillary tube, the change in the liquid level (in this case mercury is used in the capillary tube) can be followed potentiometrically. The appearance of digital densitometers on the market has simplified the determination of solution densities and, therefore, via apparent molar volumes, partial molar volumes. This technique merely requires a minimum solubility of the substance, usually $>10^{-3}$ M, as well as a high degree of purity and the substance must also be stable in solution over the time range of the measurements. Although it would be highly desirable to be able to obtain accurate density measurements under pressure, this has only been carried out in very few cases [68,69].

The compressibility of the solvent or reaction solution can be measured with a piezometer of similar design to the afore-mentioned "resistance wire" dilatometer [70—73]. Another method involves monitoring the change in the velocity of sound through the solution as a function of pressure [74].

(v) Classification of reaction mechanisms

A description of the intimate mechanism in terms of the bonding changes incurred along the reaction coordinate has been made by several authors [75—77]. According to the categories laid down by Langford and Gray [76], three stoichiometrically distinct types emerge, namely a dissociative (D) mechanism involving an intermediate of reduced coordination number; an associative (A) mechanism in which an intermediate of increased coordination number is formed; and a concerted process, or interchange (I) mechanism, involving the exchange of a ligand in the coordination sphere with one in the first solvation sphere. The (I) mechanism may be further subdivided into two classes: a dissociative interchange (I_d) in which the leaving and entering ligands are only weakly bound in the transition state; and an associative interchange (I_a) where more substantial bonding of both the leaving and entering ligands is involved. As a consequence the contributions to the energy and volume of the transition state are mainly determined by the leaving ligand in an I_d mechanism and by the entering ligand in an I_a mechanism. However, smaller contributions of the second ligand involved in the exchange cannot be neglected. Obviously this subdivision potentially includes a whole range of degrees of bonding and can therefore be difficult to define at times.

Bond stretching in a dissociative step gives rise to an increase in volume which is manifested in a decrease in the rate of reaction with increasing pressure, i.e. $\Delta V^{\neq}$ is positive. Conversely, bond formation occurring in an associative process will lead to a negative $\Delta V^{\neq}$, i.e. an increase in the rate constant with increasing pressure. For an interchange mechanism, smaller absolute values of $\Delta V^{\neq}$ may be anticipated as the effects of bond formation and cleavage counteract. However, other factors, such as the relative degrees of bond stretching and formation, the relative sizes of the ligands involved, and steric effects also contribute to the magnitude of $\Delta V^{\neq}$. Nevertheless, as a general rule, a negative $\Delta V^{\neq}$ is attributed to an I_d mechanism.

For the majority of reactions one may assume as a first approximation that the maximum possible absolute value of $\Delta V^{\neq}$ should approach the partial molar volume of either the leaving or entering ligand for a D or A mechanism, respectively. However, relaxation or expansion of the parent fragment of the complex will, amongst other factors, further modify this value. For interchange mechanisms, considerably smaller $\Delta V^{\neq}$ values can be expected, as mentioned earlier.

The effects of solvation (usually associated with electrostriction) represent another important contribution in determining the sign and magnitude of $\Delta V^{\neq}$. Therefore, the experimentally derived $\Delta V^{\neq}_{\mathrm{exp}}$ can be expressed as the sum of two terms: the intrinsic volume change $\Delta V^{\neq}_{\mathrm{intr}}$, which evolves from changes in bond lengths and angles during the activation process (this corresponds to the $\Delta V^{\neq}$ discussed in the second paragraph of this section) and is the term directly diagnostic of the intimate reaction mechanism; and the volume change resulting from solvation effects, viz. $\Delta V^{\neq}_{\mathrm{solv}}$. It should be emphasized that $\Delta V^{\neq}_{\mathrm{solv}}$ is larger in less structured solvents (e.g. benzene or carbon tetrachloride) than in highly structured ones such as water. In order to stress this point, the calculated volume changes associated with the formation of a point charge, a dipole moment and a quadrupole moment in four representative solvents are given in Table 2. Although these calculations [2] are only approximate, they are a good guide to the expected trends in the volumes of solvation, based on the dielectric constants of the solvents.

The observed $\Delta V^{\neq}_{\mathrm{exp}}$ may be dominated by the effects of solvation to the extent that even the sign of $\Delta V^{\neq}_{\mathrm{exp}}$ may differ from $\Delta V^{\neq}_{\mathrm{intr}}$. Consequently, it is often the task of the experimenter to either estimate $\Delta V^{\neq}_{\mathrm{solv}}$, or to minimize it in order to extract the more mechanistically informative $\Delta V^{\neq}_{\mathrm{intr}}$ term. Examples of both approaches will be presented for individual systems.

Stranks [17] proposed an additional approach to this problem for solvolysis reactions in that he interpreted the compressibility of activation, $\Delta\beta^{\neq}$, in terms of the migration of solvent molecules to or from the bulk solvent or first solvation sphere, from or to the coordination sphere of the complex. The intrinsic volume of activation is known to be independent of pressure at the relatively low pressures used in kinetic work [17,78]. Thus any pressure dependence of $\Delta V^{\neq}_{\mathrm{exp}}$ observed over this range must be attributed to $\Delta V^{\neq}_{\mathrm{solv}}$. In other words $\Delta V^{\neq}_{\mathrm{solv}}$, or more correctly its pressure derivative, was used to help identify the nature of the underlying reaction mechanism. Stranks went on to construct a model for a 3+ octahedral complex ion in aqueous solution in which the complex was considered to exert a centrosymmetrical electro-

TABLE 2

Volumes of solvation arising from electrostatic interactions (volumes in cm^3 mol^{-1})

Solvent	Charge (1e)	Dipole moment (10 D)	Quadrupole moment (2×10^{-25} e.s.u.)
Water	1.3	1.8	1.4
Methanol	4	6	4
Acetone	7	10	7
Benzene	27	39	28

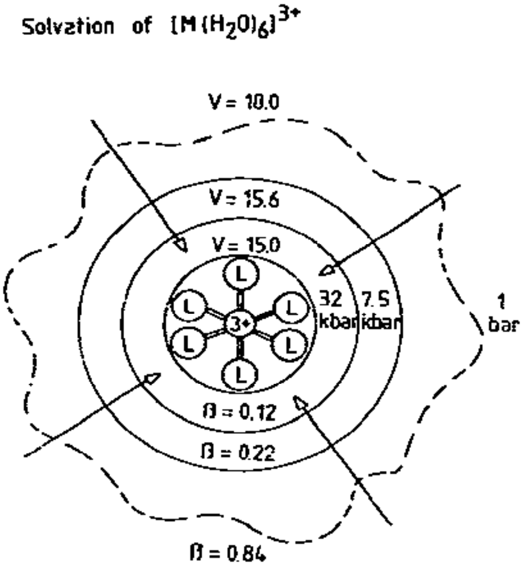


Fig. 2. Solvation model of a trivalent octahedral cation [17].

static field on the surrounding solvent. This internal pressure resulted in the formation of two solvation spheres, each containing electrostricted water molecules of reduced molar volume and compressibility, as illustrated in Fig. 2.

On the basis of this model, a D type mechanism for either a water exchange reaction or an anation reaction should exhibit a large and positive $\Delta\beta^{\neq}$ due to the diffusion of a water molecule from the relatively incompressible coordination sphere to the bulk solvent. Similarly, for an I_d mechanism $\Delta\beta^{\neq}$ should be positive, but smaller in magnitude, as the water molecule only advances to the first solvation sphere and because the reverse process now also contributes, although to a lesser extent. The converse is expected for A and I_a mechanisms, with negative $\Delta\beta^{\neq}$ values being large and small, respectively. For example, the entry of one water molecule into the coordination sphere of a 3+ complex, according to an A mechanism, would result in a $\Delta\beta^{\neq}$ of -0.72 cm^3 mol^{-1} kbar^{-1} (calculated from the β values given in Fig. 2) [17]. On the other hand, an I_a mechanism should be characterized by a $\Delta\beta^{\neq}$ of -0.1 cm^3 mol^{-1} kbar^{-1}. However it is important to note that the degree of curvature of (ln k) versus pressure plots necessary to yield $\Delta\beta^{\neq}$ values of this magnitude is very difficult to detect.

In reactions involving entering and/or leaving groups other than solvent molecules, $\Delta\beta^{\neq}$ is associated with the desolvation or increased electrostriction accompanying the migration of solvent molecules to or from the bulk solvent. In fact, the modified Tait equation mentioned earlier (eqn. (8), [36]) uses this model to calculate the number of water molecules transferred in such a process.

As a final comment on this model for the interpretation of $\Delta\beta^{\neq}$, the current view of ionic solvation favors the existence of a layer of unstructured water between the solvation spheres and the bulk water. This tends to complicate the picture presented above, which together with the observation that the initial effect of applied pressure on aqueous solutions is to desolvate the ions present [79], indicates that this model may be a somewhat misleading oversimplification. Nevertheless, in the absence of an alternative concept, Stranks' model has been used with success on a number of occasions.

B. REACTIONS OF OCTAHEDRAL COMPLEXES

(i) Solvent exchange reactions

The interpretation of the $\Delta V^{\neq}_{\text{exp}}$ for solvent exchange reactions is simplified due to the absence of complications arising from solvation changes (i.e. $\Delta V^{\neq}_{\text{exp}} \approx \Delta V^{\neq}_{\text{intr}}$) and the leaving and entering groups are the same. These reactions are therefore frequently used to characterize a particular metal center in terms of its general mechanistic behavior. In addition, the $\Delta V^{\neq}_{\text{exp}}$ for solvent exchange provides a convenient cornerstone in discussing the results of the corresponding hydrolysis and anation reactions of a given complex. This is analogous to the treatment of the respective rate constants for these reactions.

The water exchange reactions of pentaammine complexes have been well studied. Table 3 summarizes these results, including the corresponding entropies of activation.

The positive sign of $\Delta V^{\neq}_{\text{exp}}$ for the cobalt(III) complex led to the assignment of a dissociative mechanism [80]. Moreover, the small absolute value strongly suggests that the mechanism must be of the I_d type. This is consistent with the generally accepted opinion of the behavior of these complexes [36]. $\Delta\beta_0^{\neq}$ was also found to be virtually zero for all four complexes. Consequently, within the framework of Stranks' concept, an interchange mechanism was considered to hold in each case. The negative sign of $\Delta V^{\neq}_{\text{exp}}$ for the

TABLE 3

Activation parameters for the water exchange of $M(NH_3)_5OH_2^{3+}$ [a]

Complex ion	$\Delta V^{\neq}_{\text{exp}}$ ($cm^3\ mol^{-1}$)	$\Delta S^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)	T (°C)	Ref.
$Co(NH_3)_5OH_2^{3+}$	1.2 ± 0.2	28 ± 4	25/35	80
$Rh(NH_3)_5OH_2^{3+}$	−4.1 ± 0.4	3 ± 5	25	81
$Ir(NH_3)_5OH_2^{3+}$	−3.2 ± 0.1	11 ± 4	70	82
$Cr(NH_3)_5OH_2^{3+}$	−5.8 ± 0.1	0 ± 7	25	81

[a] $[HClO_4]$ = 0.01—0.1 M.

remaining three complexes was shown to be consistent with an I_a mechanism [81,82]. Furthermore, it was proposed [81,82] that cobalt(III) is indeed exceptional, in that cationic transition metal trivalent complexes can be normally expected to react via an associative mechanism.

Stranks and Swaddle [83] found $\Delta V^{\neq}_{exp}$ to be also negative (-9.3 ± 0.3 cm^3 mol^{-1} at 45°C) and $(\partial\ \Delta V^{\neq}/\partial P)_T$ close to zero, for the oxygen-18 exchange between $Cr(OH_2)_6^{3+}$ and solvent water. This result complies with the postulate of a common I_a mechanism. The relative magnitudes of $\Delta V^{\neq}_{exp}$ were considered to be mainly due to the creation of a vacancy in the solvation sheath by the incoming water molecule as it is transferred to the coordination sphere; the core of the species $ML_5OH_2^{3+}$ and $ML_5(OH_2)_2^{3+}$ were considered to have essentially the same volume [81,83]. The effect of the vacant site was thought to be greater for complexes with large, highly structured solvation sheaths. In particular, the greater acidity of the aquo ligands compared to coordinated ammonia would be expected to create a more extensive solvation sheath, thereby accounting for larger $|\Delta V^{\neq}_{exp}|$ values for $Cr(OH_2)_6^{3+}$. The order Cr > Rh > Ir parallels the order of increasing ionic radii of the metal centers and is in turn directly proportional to the extent of the solvation sheaths [82].

The volume of activation for the water exchange of $Ni(OH_2)_6^{2+}$ was found to have a pressure and temperature independent value of 7.1 ± 0.2 cm^3 mol^{-1} over the ranges of 1 to 2250 bar and 35 to 44°C [84]. An I_d mechanism is consistent with this value and with the $\Delta V^{\neq}_{exp}$ values obtained in nonaqueous solvents (discussed later in this section). Another interesting facet of this investigation [84] deals with the relaxation of pure water as a function of pressure. These results indicate that water molecules reorient faster at higher pressures due to the breakdown of the open tetrahedral structure of water.

The water exchange of *trans*-$Co(en)_2(OH_2)_2^{3+}$ was studied ($\mu = 2$ mol kg^{-1} and 25°C) up to ca. 3 kbar and a pressure-independent $\Delta V^{\neq}_{exp}$ of 5.9 ± 0.2 cm^3 mol^{-1} was reported [85]. Bond breaking was therefore assumed to dominate and an I_d mechanism proposed. Furthermore, as water exchange proceeds with retention of configuration [86], the transition state must be in the form of a tetragonal pyramid. In this regard it is particularly relevant that the isomerization equilibrium strongly favors the *cis* isomer so that a symmetrical bipyramidal intermediate for the water exchange reaction can be ruled out.

Solvent exchange in nonaqueous solvents has also been investigated under pressure for chromium(III) ions in DMSO [87] and DMF [88]. Pressure-independent, negative activation volumes were again found (i.e. -11.3 ± 1.0 cm^3 mol^{-1} at 75°C for $Cr(DMSO)_6^{3+}$ and -6.3 ± 0.2 cm^3 mol^{-1} for $Cr(DMF)_6^{3+}$ at 65.1°C), consistent with an I_a mechanism, although an A mechanism could not be completely rejected. The relative magnitudes of $\Delta V^{\neq}_{exp}$ in H_2O, DMSO and DMF were rationalized in terms of the greater importance of steric compression within the coordination sphere of the $Cr(DMSO)_6^{3+}$ ion [88]. Finally, the earlier postulate [81,82] was restated to include all trivalent cationic octahedral complexes, with the notable exception of those of cobalt-

(III), as reacting via an I_a mechanism when the ionic radius of the central metal is greater than 60 pm, although very large trivalent ions could react according to an I_d mechanism.

In DMSO the solvent exchange reaction of $Co(NH_3)_5DMSO^{3+}$ is accompanied by either internal redox to cobalt(II) or rapid substitution of the conjugate base of this complex [89]. However, in the presence of added acid these complicating effects are virtually eliminated and $\Delta V^{\neq}_{exp}$ for exchange is 10.0 ± 1.2 $cm^3\ mol^{-1}$ at 45°C. The large positive value of $\Delta V^{\neq}_{exp}$ shows that Co—DMSO bond breaking is the dominant contribution, thereby confirming the assignment of an I_d mechanism to the solvent exchange of cobalt(III) complexes. The solvent exchange reactions of $Co(NH_3)_5DMF^{3+}$ and $Rh(NH_3)_5DMF^{3+}$ in acidic DMF yielded volumes of activation of 3.2 ± 1.2 $cm^3\ mol^{-1}$ at 55.4°C and —1.4 ± 0.2 $cm^3\ mol^{-1}$ at 44.8°C, respectively [90]. The entropies of activation also show a parallel tendency, i.e. 40 ± 1 and —20 ± 6 $J\ K^{-1}\ mol^{-1}$. Therefore, as in the water exchange reactions of the respective cobalt(III) and rhodium(III) complexes, I_d and I_a mechanisms were assigned to these reactions in DMF. The small value of $\Delta V^{\neq}_{exp}$ for $Rh(NH_3)_5DMF^{3+}$ was suggested to be due to the counteracting effects of Rh—DMF bond stretching, as well as possible expansion of the remaining Rh—N bonds.

A detailed PMR high pressure investigation of the solvent exchange of $[MS_6](ClO_4)_2$, where M = Ni(II) or Co(II) and S = DMF, CH_3CN or CH_3OH was recently carried out [91]. Since the $\Delta\beta^{\neq}$ values were found to be small, the rate data were fitted according to the usual linear relationship (eqn. (1)) and to the polynomial form (eqn. (4)). As shown in Table 4, positive $\Delta V^{\neq}_{exp}$ values were obtained from both treatments and, together with the small and generally positive $\Delta\beta^{\neq}$ values, provide strong support for an I_d mechanism. Conceivably, the extreme $\Delta V^{\neq}_{exp}$ values are $-V^0$ and $+V^0$ (V^0 being the partial molar volume of the solvent). The authors [91] consequently used the dimen-

TABLE 4

Activation volumes for the solvent exchange of $M(solvent)_6^{3+}$ [91]

M	Solvent	T (°C)	$\Delta V^{\neq}_{exp}$ [a] ($cm^3\ mol^{-1}$)	$\Delta V^{\neq}_{exp}/V^0$	$\Delta V^{\neq}_{exp}$ [b] ($cm^3\ mol^{-1}$)	$\Delta\beta^{\neq}_0$ ($cm^3\ mol^{-1}\ kbar^{-1}$)
Ni^{2+}	CH_3OH	34	11.4 ± 0.6	0.28	13.0 ± 1.6	2.0 ± 2.0
	DMF	24	9.1 ± 0.3	0.12	10.1 ± 0.9	1.0 ± 1.0
	CH_3CN	21	9.6 ± 0.3	0.18	11.3 ± 1.0	1.8 ± 1.0
Co^{2+}	CH_3OH	6	8.9 ± 0.3	0.22	10.9 ± 0.7	2.0 ± 0.7
	DMF	23	6.7 ± 0.3		8.4 ± 0.8	1.4 ± 0.7
		—20	9.2 ± 0.3	0.12	9.9 ± 0.8	0.8 ± 0.9
	CH_3CN	—13	9.9 ± 0.7	0.20	8.2 ± 2.3	—1.7 ± 2.2 [c]

[a] Calculated from the linear equation. [b] Calculated from the quadratic equation. [c] Negative sign is not meaningful due to large uncertainty.

TABLE 5

Activation parameters for the ligand exchange reactions of $MX_5L + L^* \rightleftharpoons MX_5L^* + L$ in CH_2Cl_2 [92]

MX_5L	T (°C)	$\Delta V^{\neq}_{exp}$ ($cm^3\ mol^{-1}$)	$\Delta V^{\neq}_{calc}$ ($cm^3\ mol^{-1}$)	$\Delta\beta^{\neq}$ ($cm^3\ mol^{-1}\ kbar^{-1}$)
$NbCl_5Me_2O$	13.1, 30.0	28.7 ± 1.1	26.8	6.6 ± 1.2
$NbCl_5MeCN$ [a]	13.0	19.5 ± 1.6	13.3	0.7 ± 1.6
$NbCl_5Me_3CCN$ [a]	14.2	15.2 ± 1.7	13.3	2.0 ± 1.5
$NbCl_5(MeO)Cl_2PO$ [a]	11.5, 24.4	10.5 ± 0.7	17.3	3.7 ± 0.7
$NbCl_5(Me_2N)_3PS$	34.2	17.7 ± 1.4 [b]	17.0	
$TaCl_5Me_2O$	36.9	27.8 ± 1.2	26.8	8.3 ± 1.3
$TaBr_5Me_2O$ [c]	10.6	30.5 ± 0.8	31.0	6.5 ± 0.7
$TaCl_5Me_2S$	10.6	−19.8 ± 0.9		−5.3 ± 0.3
$TaCl_5Me_2Se$	14.3	−18.7 ± 1.0		−5.9 ± 0.3
$TaCl_5Me_3Te$	11.5	−10.7 ± 0.8 [b]		
$NbBr_5Me_2S$	6.7	−12.1 ± 1.0		−4.2 ± 1.0
$TaBr_5Me_2S$	12.4, 21.0	−12.6 ± 0.8		−0.3 ± 0.7
$TaBr_5Me_2Se$	12.0	−13.6 ± 0.8		
$TaBr_5Me_2Te$	33.8	−16.4 ± 0.7		−3.1 ± 0.7

[a] The solvent was $CHCl_3$. [b] A linear fit was used. [c] Taken from ref. 93.

sionless parameter $\Delta V^{\neq}_{exp}/V^0$ as a more sensitive guide to the nature of the interchange process. An average $\Delta V^{\neq}_{exp}/V^0$ of ca. 0.17 complies with the definition of an I_d mechanism. It was also pointed out that the errors in $\Delta S^{\neq}$ values for solvent exchange with paramagnetic ions obtained from NMR measurements are frequently so large as to prevent any correlation with reaction mechanism. The smaller values of $\Delta V^{\neq}_{exp}/V^0$ for the cobalt(II) complexes and the faster rate of solvent exchange compared to the analogous Ni(II) complexes, led to the conclusion that the cobalt(II) reaction is less dissociative in character.

(ii) Ligand exchange reactions

Merbach and Vanni [92] used high resolution NMR to monitor the reaction

$$MX_5L + {}^*L \rightleftharpoons MX_5{}^*L + L \qquad (10)$$

where M = Nb or Ta and X = Cl or Br. The results of these high pressure studies, shown in Table 5, clearly demonstrate that a "dissociative—associative mechanistic crossover" occurs in this system. The impressive change in the sign of $\Delta V^{\neq}_{exp}$ (this change is also reflected in the $\Delta S^{\neq}$ values, with one exception) establishes that a dissociative mechanism is operative in the first seven reactions listed in Table 5 ($\Delta V^{\neq}_{\text{exp}}$ is positive), while the remaining negative $\Delta V^{\neq}_{\text{exp}}$ values are in keeping with an associative process. The interpretation of these values is simplified by the fact that the reactants and the transition state are neutral and, by definition, the entering and leaving groups are identical. Thus, $\Delta V^{\neq}_{\text{exp}}$ was considered to be negligible. By assuming that the positive $\Delta V^{\neq}_{\text{exp}}$ values correspond to a D mechanism, an activation volume ($\Delta V^{\neq}_{\text{calc}}$) was estimated using the following boundary condition. The volume $\overline{V}(MX_6)$ equals $\overline{V}(MX_5)$ and can be estimated by assuming the molecule to be a solid sphere whose radius is determined by the van der Waals radii of the constituent X ligands, with the metal ion occupying the central hole. The estimated volume of activation is then equivalent to the volume within the first coordination sphere that is filled by the exchanging ligand. Considering the simplicity of this model the agreement between $\Delta V^{\neq}_{\text{exp}}$ and $\Delta V^{\neq}_{\text{calc}}$ is very good and can be taken as direct evidence of a D mechanism for these particular reactions.

A similar treatment of an associative process was considered impractical due to the unknown effects that steric crowding within a seven-coordinate transition state would have on $\Delta V^{\neq}_{\text{calc}}$. However, the relatively small magnitudes of $\Delta V^{\neq}_{\text{exp}}$, i.e. 11 to 20 cm^3 mol^{-1}, led the authors [92] to favor an I_a mechanism over an A mechanism, although the latter could not be ruled out. In fact the finite negative $\Delta\beta^{\neq}$ values may suggest an A mechanism.

(iii) Hydrolysis reactions

The most studied and inherently simplest system involves the aquation reactions of acidopentaamminecobalt(III) complexes [36,94–96],

$$Co(NH_3)_5X^{(3-n)+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + X^{n-} \qquad (11)$$

These reactions were studied in acidic solutions in order to minimize any contribution from the more facile base hydrolysis. The complete activation volume data are summarized in Table 6.

The $\Delta V^{\neq}_{\text{exp}}$ values calculated by the two different methods are virtually the same within the given experimental error limits. For X = Cl [95], NCS and DMSO, where larger errors were incurred, application of such equations is unrealistic and a linear treatment was favored in order to obtain a minimum $|\Delta V^{\neq}_{\text{exp}}|$ value.

Although the negative activation volumes (with the exception of X = N_3, which is a special case involving acid catalysis) are not immediately indicative of the expected I_d mechanism, the large changes in electrostriction, which stem from the creation of charge as the Co—X bond is stretched, now represented an important, if not the dominant, contribution to $\Delta V^{\neq}_{\text{exp}}$. This is exemplified in the large negative $\Delta V^{\neq}_{\text{exp}}$ for SO_4^{2-} as leaving ligand compared to +1.2 cm^3 mol^{-1} [80] for the water exchange of $Co(NH_3)_5OH_2^{3+}$.

A linear relationship exists between the $\Delta V^{\neq}_{\text{exp}}$ values for X = Cl, Br, NO_3,

TABLE 6

Activation volumes for the aquation of $Co(NH_3)_5X^{(3-n)+}$ (25°C, $\mu = 0.1$ M, $[H^+] = 5 \times 10^{-5}$ M)

X^{n-}	$\Delta V^{\neq}_{exp}$ [a] ($cm^3\ mol^{-1}$)	$\Delta\beta^{\neq}_0$ ($cm^3\ mol^{-1}\ kbar^{-1}$)	$\Delta V^{\neq}_{exp}$ [b] ($cm^3\ mol^{-1}$)	x	Ref.
Cl^-	−7.5 ± 1.0 [c,d]				95
	−9.9 ± 0.5	2.1 ± 0.2	−10.6 ± 0.4	4	36
Br^-	−8.7 ± 0.2	2.0 ± 0.2	−9.2 ± 0.2	4	36
NO_3^-	−5.9 ± 0.4	1.0 ± 0.2	−6.3 ± 0.4	2	36
SO_4^{2-}	−17.0 ± 0.6	4.1 ± 0.5	−18.5 ± 0.7	8	36
NCS^-	−4.0 ± 1.0 [c,e]				36
N_3^-	+16.0 ± 0.4 [f]	−2.1 ± 0.3 [f]	+16.8 ± 0.5 [f]	−4	36
DMSO	−1.7 ± 0.7 [c]				96

[a] Calculated from the quadratic expression (eqn. (4)). [b] Calculated from the modified Tait expression (eqn. (8)). [c] Calculated from the linear equation. [d] 59.8°C and $\mu \simeq [H^+] = 0.1$ M. [e] 88.0°C. [f] 75.0°C.

SO_4, DMSO and H_2O and the corresponding $\Delta\overline{V}$ values which were for the most part reported by Spiro et al. [97]. The slope of the line is approximately unity which indicates that the departing X^{n-} ligand must be almost as fully dissociated in the transition state as in the final product. This concept is reminiscent of the free energy relationship often used in kinetic studies.

As defined earlier, the positive values of x given in Table 6 correspond to the increase in the number of water molecules solvating the complex and leaving group during the activation process according to the treatment of Jones et al. [36]. In other words, x is a direct quantitative measure of the increase in electrostriction as exemplified by the largest value for x being found for the sulfato complex. Furthermore, a plot of $\Delta V^{\neq}_{exp}$ against x gave a smooth curve with a slope at $x = 0$ of -3.1 cm^3 mol^{-1} so that for X = H_2O the molar volume of water in the first solvation sphere amounts to $18.0 - 3.1 = 14.9$ cm^3 mol^{-1}. Taking V^0 for H_2O in the coordination sphere of $Co(NH_3)_5OH_2^{3+}$ to be 14.0 ± 0.3 cm^3 mol^{-1}, it was argued [36] that a $\Delta V^{\neq}_{exp}$ for water exchange of 1.2 cm^3 mol^{-1} originates from the difference in the volumes of water in the first two spheres surrounding the Co(III) center, i.e. this complies with the definition of an I_d mechanism.

Another approach to these reactions was made by determining the partial molar volumes of the species involved and then constructing a volume equation [96]. If the pentamminecobalt(III) fragment and the leaving ligand are assumed to be fully solvated in the transition state, as indicated by the close agreement of $\Delta V^{\neq}_{exp}$ and $\Delta\overline{V}$, then $\Delta V^{\neq}_{exp}$ may be expressed as

$$\Delta V^{\neq}_{exp} = \overline{V}\{Co(NH_3)_5^{3+}\} + \overline{V}\{X^{n-}\} - \overline{V}\{Co(NH_3)_5X^{(3-n)+}\} \qquad (12)$$

This equation can be rewritten to yield the value of $\overline{V}\{Co(NH_3)_5^{3+}\}$ which must be constant if a D mechanism were valid. Indeed, for X = Cl, Br, NO_3, SO_4, DMSO and H_2O a mean value of 54.9 ± 0.9 cm^3 mol^{-1} was obtained for the volume of the common five-coordinate species. Moreover, Stranks [17] estimated the intrinsic volume of $Ni(NH_3)_6^{2+}$ to be equal to that of a hypothetical $Ni(NH_3)_5^{2+}$ species to within 0.1 cm^3 mol^{-1}. Thus the stable complex $Co(NH_3)_6^{3+}$ should be a good model for the pentacoordinate transition state species. The molar volume of the former is 55.1 ± 1.1 cm^3 mol^{-1} which is in excellent agreement with the mean value of $\overline{V}\{Co(NH_3)_5^{3+}\}$, thereby substantiating this concept further. Stranks' hypothesis, as well as the partial molar volume data on which the calculation of $\overline{V}\{Co(NH_3)_5^{3+}\}$ is based, was recently criticized by Swaddle [98].

For X = NCS a $\Delta V^{\neq}_{exp}$ of 1.4 cm^3 mol^{-1} was calculated in contrast to the measured value of −4.0 ± 1.0 cm^3 mol^{-1}. However, the latter was measured at 88°C so that reversibility of the reaction and decomposition of NCS^- at these temperatures [36], coupled with the temperature dependence of the molar volumes could easily account for the discrepancy. Similarly, for X = N_3 temperature differences are significant, but by assuming that the leaving group is in fact N_3H, the molar volumes are consistent with an acid catalyzed aquation [96].

High pressure studies of the aquation of the corresponding chromium(III) and rhodium(III) complexes are more limited [64,95,96,99], as can be seen from the data summarized in Table 7. Plots of $\Delta V^{\neq}_{exp}$ (chromium(III)) versus either $\Delta V^{\neq}_{exp}$ for the corresponding cobalt(III) complexes where the Co—X bond is believed to be essentially broken, or $\Delta \overline{V}$ for the chromium(III) reactions are linear with slopes of ca. 0.5 [64]. It was concluded that bond stretching was only half as advanced in the chromium(III) system and an I_a mechanism was proposed [64], in keeping with the assignment of this mechanism to the analogous water exchange reaction. Supporting evidence was later provided [96] from the molar volumes which were shown not to comply with the treatment used on the cobalt(III) complexes, i.e. by assuming $\overline{V}\{Cr$-

TABLE 7

Volume data for the aquation of $Cr(NH_3)_5X^{(3-n)+}$ and $Rh(NH_3)_5NO_3^{2+}$ (25°C; μ = 0.1 M; units: $\Delta V^{\neq}$ cm^3 mol^{-1} and $\Delta\beta_0^{\neq}$ cm^3 mol^{-1} $kbar^{-1}$)

X^{n-}	$\Delta V^{\neq}_{exp}$	$\Delta\beta_0^{\neq}$	Ref.	$\Delta V^{\neq}_{D}$	$\Delta V^{\neq}_{A}$
Chromium					
Cl^-	−10.8 ± 0.3	1.0 ± 0.2	64	7.2	−14.4
Br^-	−10.2 ± 0.3	1.0 ± 0.1	64	6.1	−13.3
I^-	−9.4 ± 0.3	1.0 ± 0.1	64	12.5	−15.7
NCS^-	−8.6 ± 1.0 [a,b]		95	11.7	−14.5
Rhodium					
NO_3^-	−6.9 ± 0.4 [b,c]		99	1.7	−9

[a] 79.8°C. [b] Calculated from the linear equation. [c] 40°C.

TABLE 8

Activation parameters for the aquation of *trans*-$CoN_xCl_2^+$ in 0.01 M [HNO_3] and μ = 0.1 M [101]

N_x	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	T (°C)	$\Delta V^{\neq}_{exp}$ (cm^3 mol^{-1})
$(NH_3)_4$	86.6	−6	10	−1.7 ± 0.7
	101.2 [a]	44 [a]	25	−1.3 ± 0.3
$(en)_2$	111.7	44	30	−1.1 ± 0.9
	100.0 [a]	5 [a]	25	−1.7 ± 1.1 [a]
$(en)_2$ [b]	88.0	−18	30	−0.3 ± 0.4
$(Meen)_2$	111.1	36	30	−3.1 ± 0.5
$(Eten)_2$	94.5	−6	30	−0.3 ± 0.9
$(Pren)_2$	113.1	55	30	0.3 ± 0.6
RS-(2.3.2.tet)	103.5	8	25	−0.8 ± 1.7
	109.8 [a]	32 [a]	50	−1.3 ± 0.4 [a]
			30	−1.0 ± 0.4
RR,SS-(2.2.2.tet)	108.3 [c]	50 [c]	25	1.0 ± 0.4
(3.2.3.tet)	106.1	29	25	−2.8 ± 1.5
(cyclam)	76.5 [c]	−26 [c]	50	−2.1 ± 0.9

[a] These reactions were conducted in pure water. [b] These results are for the *cis* isomer.
[c] Ref. 102: [HNO_3] = 0.01 M, μ = 0.011 M.

$(NH_3)_5^{3+}\} = \bar{V}\{Cr(NH_3)_6^{3+}\}$ = 68.6 cm^3 mol^{-1}, volumes of activation, $\Delta V^{\neq}_D$, were estimated according to eqn. (12) and are shown in Table 7. If it is accepted that the dissociative process is only 50% complete in the transition state and can be represented by 0.5 $\Delta V^{\neq}_D$, then $\Delta V^{\neq}_A$ is the contribution from Cr—OH_2 bond formation necessary to attain the observed $\Delta V^{\neq}_{exp}$. The consistency of the $\Delta V^{\neq}_A$ values, as well as their negative sign and absolute values close to the volume of a water molecule in the first solvation sphere of a 2+ complex ion, strongly endorse the assignment of an I_a mechanism.

For the $Rh(NH_3)_5NO_3^{2+}$ complex, $\Delta V^{\neq}_{exp}$ is virtually equal to that for the analogous cobalt(III) complex. However, application of eqn. (12) yielded a $\Delta V^{\neq}_D$ totally inconsistent with a basically dissociative mechanism [99]. The smaller $|\Delta V^{\neq}_A|$ value may indicate that the reaction mechanism is a pure interchange process (I) with bond breaking and formation only 50% complete in the transition state, although more measurements are required to substantiate this hypothesis.

The aquation of $Cr(OH_2)_5I^{2+}$ was studied up to ca. 2.5 kbar and a pressure-independent $\Delta V^{\neq}_{exp}$ of −5.4 ± 0.4 cm^3 mol^{-1} (25°C) was recorded [100]. From dilatometric measurements, a $\Delta\bar{V}$ of −3.3 ± 0.3 cm^3 mol^{-1} was determined. In view of the fact that $\Delta V^{\neq}_{exp} < \Delta\bar{V}$, an I_a mechanism was again favored for this chromium(III) cation.

The aquation of a series of cobalt(III) complexes of the general form, *trans*-$CoN_xCl_2^+$, has been studied in detail [101] and the results are summarized in Table 8. This system presents the added complication by containing two potential leaving ligands, although loss of the second chloride is *significantly* slower than the rate-determining dissociation of the first. It is immediately apparent that neither the nature of the amine ligand, nor temperature, nor the medium, have any significant effect on $\Delta V^{\neq}_{exp}$. Moreover, the *cis* and *trans* isomers of $Co(en)_2Cl_2^+$ exhibit a common $\Delta V^{\neq}_{exp}$. Thus the rather large fluctuations in $\Delta S^{\neq}$ are not reflected in the $\Delta V^{\neq}_{exp}$ values which are virtually zero and pressure insensitive within the experimental error limits. By comparison, the water exchange of *trans*-$Co(en)_2(OH_2)_3^{2+}$ yielded a $\Delta V^{\neq}_{exp}$ of 5.9 ± 0.2 cm^3 mol^{-1} which was mainly ascribed to bond breaking with little or no change in solvation and the transition state was considered to be a tetragonal pyramid [85]. The same mechanism apparently applies to the dichloro analogues with a negative $\Delta V^{\neq}_{solv}$ term arising from charge development in the transition state compensating for the positive $\Delta V^{\neq}_{intr}$ term. Furthermore, Stranks and Vanderhoek [103] measured a $\Delta V^{\neq}_{exp}$ for the isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ of 14.3 ± 0.2 cm^3 mol^{-1} with $-(\partial\, \Delta V^{\neq}_{exp}/\partial P)_T = 1$ cm^3 mol^{-1} $kbar^{-1}$ which was considered as strong evidence for a D mechanism involving a trigonal-bipyramidal five-coordinate intermediate. Therefore, the aquation of the dichloro complexes appears more consistent with a tetragonal-pyramidal intermediate so that in these cases where *cis* products are observed (e.q. N_x = $(NH_3)_4$ or $(en)_2$ or RR,SS-(2.3.2.tet)), rearrangement of this intermediate must occur after the rate-determining step.

The molar volume of a trigonal-bipyramidal five-coordinate species may be assumed to be similar to that of an octahedral six-coordinate complex, provided the ejected ligand is not much larger than the remaining ligands. Therefore, dissociative processes involving this configuration in the transition state should have a $\Delta V^{\neq}_{exp}$ approaching the molar volume of the leaving group in the absence of strong solvation contributions. The molar volume of a tetragonal-pyramidal species must be significantly smaller than the parent octahedral molecule under the same conditions, with the result that the $\Delta V^{\neq}_{exp}$ for this reaction should be considerably less than the molar volume of the leaving group. This qualitative argument is in keeping with the mechanism assignments given above.

It is significant that the volumes of activation for the aquation of *trans*-$Co(en)_2Br_2^+$ and *trans*-$Co(2.3.2.tet)Br_2^+$ are more positive than their dichloro counterparts, i.e. 1.4 ± 0.6 and 3.4 ± 0.6 cm^3 mol^{-1}, respectively [101]. This tendency stems from either a larger $\Delta V^{\neq}_{intr}$ due to the larger cross-sectional area of the departing bromide ligand, or a smaller $|\Delta V^{\neq}_{solv}|$ due to reduced electrostriction for the bromide ion, or a combination of both these effects.

Steric strain within the amine ligand, in particular the chelated tetraammine ligands, is manifested in the rate constants and $\Delta S^{\neq}$ values. This was clearly demonstrated by Eade et al. [104] who found that a linear correlation exists between the rate constants for aquation of a series of cobalt(III) complexes and N—Co—N bending frequencies observed in the far-IR spectrum. The series was recently extended to other cobalt(III) complexes [101] and with the expected exception of *trans*-$Co(NH_3)_4Cl_2^+$, which contains the only

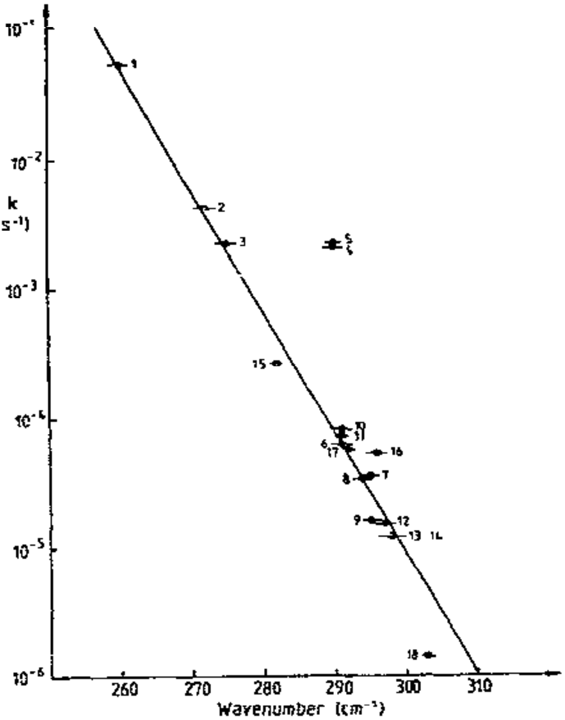


Fig. 3. Correlation between log *k* of the hydrolysis reactions of $Co(N_4)Cl_2^+$ and the N—Co—N deformation frequency [101,104]. Key: 1, *trans*-$[Co(tmd)_2Cl_2]ClO_4$[a]; 2, *trans*-$[Co(sbn)_2Cl_2]ClO_4$[a]; 3, *trans*-$[Co(ibn)_2Cl_2]ClO_4$[a]; 4, *trans*-$[Co(NH_3)_4Cl_2]Cl$[a]; 5, *trans*-$[Co(NH_3)_4Cl_2]Cl$[b]; 6, *trans*-$[Co(pn)_2Cl_2]ClO_4$[a]; 7, *trans*-$[Co(en)_2Cl_2]ClO_4$[a]; 8, *trans*-$[Co(en)_2Cl_2]Cl$[b]; 9, *trans*-$[Co(Meen)_2Cl_2]Cl$[b]; 10, *trans*-$[Co(Eten)_2Cl_2]Cl$[b]; 11, *trans*-$[Co(Pren)_2Cl_2]Cl$[b]; 12, *trans*-$[Co(2.3.2\text{-tet})Cl_2]Cl$[a]; 13, *trans*-$[Co(RS\text{-}2.3.2\text{-tet})Cl_2]Cl$[b] 14, *trans*-$[Co(RS\text{-}2.3.2\text{-tet})Cl_2]ClO_4$[b]; 15, *trans*-$[Co(RR,SS\text{-}2.3.2\text{-tet})Cl_2]ClO_4$[c]; 16, *trans*-$[Co(2.3.2\text{-tet})Cl_2]ClO_4$[a]; 17, *trans*-$[Co(3.2.3\text{-tet})Cl_2]Cl$[b]; 18, *trans*-$[Co(cyclam)Cl_2]Cl$[a].
[a] 0.1 M HNO_3; [b] 0.01 M HNO_3, $\mu = 0.1$ M; [c] pH = 2, $\mu = 0.014$ M.

monodentate amine ligands, the relationship was confirmed, as illustrated in Fig. 3. However, the conformation of the inert ligand(s) need not necessarily affect $\Delta V^{\neq}_{exp}$, which explains the insensitivity of this parameter to variations in N. In other words, volume changes result from the translation and rotation of the species involved.

Twigg [105] claimed that $\Delta S^{\neq}$ and $\Delta V^{\neq}_{exp}$ are related by establishing that a linear relationship exists between these two parameters for a series of aquation reactions. However, the scatter was quite large and when the more recent data are included, as shown in Fig. 4, the relationship can be seen to be purely qualitative. Indeed, no thermodynamic or quasithermodynamic equation links the two directly, although it may be generally argued that they stem from similar sources (keeping in mind the discussion in the previous

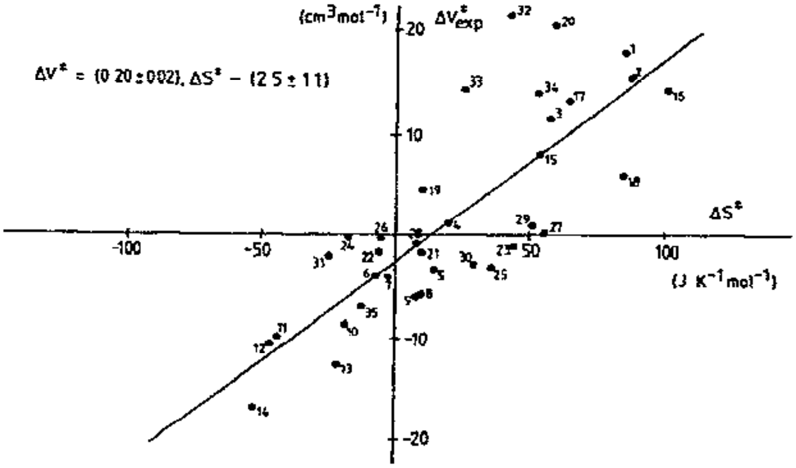


Fig. 4. $\Delta V^{\neq}_{\rm exp}$ versus $\Delta S^{\neq}$ for acid aquation and water exchange reactions of low-spin d^3 and d^6 complexes. Points 1—20 were taken from the original plot [105]. Key: 1, Fe$(NO_2\text{-phen})_3^{2+}$; 2, Fe$(\text{phen})_3^{2+}$; 3, Fe$(Me_2\text{-phen})_3^{2+}$; 4, $Co(NH_3)_5OH_2^{3+}$; 5, $Ir(NH_3)_5OH_2^{3+}$; 6, $Co(NH_3)_5NCS^{2+}$; 7, $Rh(NH_3)_5OH_2^{3+}$; 8, $Cr(NH_3)_5OH_2^{3+}$; 9, $Co(NH_3)_5NO_3^{2+}$; 10, $Co(NH_3)_5Br^{2+}$; 11, $Co(NH_3)_5Cl^{2+}$; 12, $Cr(NH_3)_5Cl^{2+}$; 13, $Cr(OH_2)_5NO_3^{2+}$; 14, $Co(NH_3)_5SO_4^+$; 15, *trans*-Co$(en)_2(SeO_3H)OH_2^{2+}$; 16, *trans*-Co$(en)_2(OH_2)_2^{3+}$; 17, *trans*-Co$(en)_2(OH)_2^{+}$; 18, *trans*-Co$(en)_2(OH_2)_2^{3+}$; 19, Co$(en)_2(OH)OH_2^{2+}$; 20, $Fe(CN)_5(3,5\text{-}Me_2py)^{3-}$; 21, $Co(NH_3)_5DMSO^{3+}$; 22, *trans*-$Co(NH_3)_4Cl_2^+$; 23, *trans*-Co$(en)_2Cl_2^+$; 24, *cis*-Co$(en)_2Cl_2^+$; 25, *trans*-Co$(Meen)_2Cl_2^+$; 26, *trans*-Co$(Eten)_2Cl_2^+$; 27, *trans*-Co$(Pren)_2Cl_2^+$; 28, *trans*-Co(RS-2.3.2-tet)Cl_2^+; 29, *trans*-Co(RR,SS-2.3.2-tet)Cl_2^+; 30, *trans*-Co(3.2.3-tet)Cl_2^+; 31, *trans*-Co(cyclam)Cl_2^+; 32, $RhCl_6^{3-}$; 33, $RhCl_5OH_2^{2-}$; 34, $Co(CN)_5I^{3-}$; 35, $Rh(NH_3)_5NO_3^{2+}$.

paragraph) and therefore usually possess the same sign. Consequently, to use such a relationship as an indication of the nature of the contributing interactions appears advantageous, but to circumvent independent kinetic measurements with predicted activation parameters can be misleading and detracts from the overall goal of kinetic measurements, which is to diagnose the underlying mechanism, using all the available information.

Although the majority of octahedral complexes are cationic, a number of isolated high pressure studies have been devoted to anionic complexes. Volumes of activation for the aquation of $Cr(NCS)_6^{3-}$ and $Cr(NH_3)_2(NCS)_4^-$ were reported to be 16 ± 2 and −2.4 ± 0.8 cm³ mol⁻¹ at 50°C, respectively [106]. The former was found to be strongly pressure dependent with $\Delta\beta_0^{\neq}$ ca. −15 ± 5 cm³ mol⁻¹ kbar⁻¹, while $\Delta V^{\neq}_{\rm exp}$ for the second reaction was virtually independent of pressure. These results were interpreted [106] in terms of an I_d mechanism for the $Cr(NCS)_6^{3-}$ complex, involving at least one water molecule, whereas the aquation of $Cr(NH_3)_2(NCS)_4^-$ was described as involving an "S_N2 front-side process", i.e. an A mechanism. Although these assignments confirmed the conclusions of previous workers [107—109], an extension of Stranks' model [17] to anionic complexes would appear to favor a D mechanism for the former reaction and an I_a mechanism, or even an I_d, for the latter.

It must be noted that dissociation of a thiocyanato ligand only results in a moderate charge separation and therefore a limited change in electrostriction or a small positive contribution to $\Delta V^{\neq}_{\mathrm{exp}}$, estimated at 5 cm^3 mol^{-1} by Gay and Nalepa [106]. The aquation of $\mathrm{Cr(NCS)_6^{3-}}$ was subsequently reinvestigated [110] and a $\Delta V^{\neq}_{\mathrm{exp}}$ of 2.9 ± 0.8 cm^3 mol^{-1} at 25°C was recorded. Moreover, it was found to be pressure independent. Thus it was argued that the positive contributions of Cr—NCS bond stretching and the associated decrease in electrostriction are somewhat compensated by the effect of Cr—$\mathrm{OH_2}$ bond formation, consistent with an $\mathrm{I_d}$ mechanism. Langford and Tong [111] suggested that a dissociative mechanism can occur in reactions of chromium(III) complexes in which strong *trans*-labilizing ligands, such as NCS, are present. They also established that specific solvation sites are evident and tend to influence the mode of activation of chromium(III) complexes.

The aquation of cobalt(III) complexes of the type $\mathrm{Co(CN)_5X^{n-}}$ is generally accepted as involving a limiting dissociative mechanism with a five-coordinate intermediate $\mathrm{Co(CN)_5^{2-}}$. Accordingly, positive volumes of activation were found [112] for X = Cl, Br, I and $\mathrm{N_3}$ at 40°C and μ = 1 M, i.e. 7.8 ± 0.5, 7.6 ± 0.6, 14.0 ± 0.7 and 16.8 ± 0.5 cm^3 mol^{-1}, respectively. The latter reaction was measured in 0.1 M $\mathrm{HClO_4}$ so that acid-catalyzed aquation was predominant. For the remaining reactions a D mechanism would result in a small positive value for $\Delta V^{\neq}_{\mathrm{solv}}$ due to charge separation and specific solvation of X, with the bulk of $\Delta V^{\neq}_{\mathrm{exp}}$ being derived from $\Delta V^{\neq}_{\mathrm{intr}}$ which varies directly with the cross-sectional area of the leaving ligand. The molar volumes of the two substrates $\mathrm{Co(CN)_5Cl^{3-}}$ and $\mathrm{Co(CN)_5Br^{3-}}$ were measured at 127.5 and 136.5 cm^3 mol^{-1} so that with V^0 (Cl$^-$) = 21.7$_5$ cm^3 mol^{-1} and V^0(Br$^-$) = 29.4 cm^3 mol^{-1}, application of eqn. (12) yielded 114 and 115 cm^3 mol^{-1}, respectively, for the volume of the $\mathrm{Co(CN)_5^{2-}}$ species [112]. The similarity between these two values was considered as evidence for a D mechanism.

In acidic solution the stepwise aquation of $\mathrm{RhCl_6^{3-}}$ yielded exclusively "*cis*" products with the final stable species being *fac*-$\mathrm{RhCl_3(OH_2)_3}$ [113]. Based on the results of an earlier chloride exchange study of the first aquation step [114] and on the steric course of these reactions, a D mechanism was proposed in which the five-coordinate intermediate has a square-pyramidal structure [113]. The volumes of activation for the aquation of $\mathrm{RhCl_6^{3-}}$ and $\mathrm{RhCl_5OH_2^{2-}}$ proved to be accordingly large and positive, viz. 21.5 ± 0.6 and 14.3 ± 0.5 cm^3 mol^{-1}, respectively, at 20°C and μ = [$\mathrm{HClO_4}$] = 4 M [115]. The former value increased only slightly at lower ionic strength, 24.5 ± 0.3 cm^3 mol^{-1}, μ = 1 M. These values were therefore considered to underline that the mechanism must be dissociative, most probably of the D type.

Until now aquation reactions have been presented for which the leaving ligand was unidentate. However some examples exist in which bidentate leaving groups are involved. This group of reactions includes the acid-hydrolysis of $\mathrm{M(C_2O_4)_3^{3-}}$, where M = Co(III), Cr(III) and Rh(III). The respective volumes of activation were found to be 10.8 ± 0.4 (50° C), —6.3 ± 0.4 (50° C) and —7.9 ± 0.6 (60° C) $cm^3 mol^{-1}$ at $[H^+] = 1$ M [116]. Although these results are indicative of two extremely different processes involving the cobalt(III) complex on the one hand and the chromium(III) and rhodium(III) complexes on the other, these reactions are complicated, as can be seen from the rate expression

$$k_{obs} = k'_1 + k'_2[H^+] + k'_3[H^+]^2 \tag{13}$$

The sequence of equilibria and rate-determining steps consistent with this rate equation are

$$M(C_2O_4)_3^{3-} + H_2O \overset{K_1}{\rightleftharpoons} M(C_2O_4)_2(OC_2O_3)(OH_2)^{3-} \tag{14}$$

$$M(C_2O_4)_3^{3-} + H_3O^+ \overset{K_2}{\rightleftharpoons} M(C_2O_4)_2(OC_2O_3H)(OH_2)^{2-} \tag{15}$$

$$M(C_2O_4)_2(OC_2O_3)(OH_2)^{3-} + H_2O \xrightarrow{k_1} M(C_2O_4)_2(OH_2)_2^- + C_2O_4^{2-} \tag{16}$$

$$M(C_2O_4)_2(OC_2O_3H)(OH_2)^{2-} + H_2O \xrightarrow{k_2} M(C_2O_4)_2(OH_2)_2^- + C_2O_4H^- \tag{17}$$

$$M(C_2O_4)_2(OC_2O_3H)(OH_2)^{2-} + H_3O^+ \xrightarrow{k_3} M(C_2O_4)_2(OH_2)_2^- + C_2O_4H_2 \tag{18}$$

These equations all refer to *cis* isomers. The complexity of the acid dependence of k_{obs}, and hence the overall $\Delta V^{\neq}_{exp}$, allowed only a semi-quantitative treatment of the volumes of activation to be made, although the absence of k'_3 from eqn. (13) for cobalt and k'_1 for chromium and rhodium simplified the situation slightly [116]. By assuming $\Delta V^{\neq}(k_1) = \Delta V^{\neq}(k_2)$ and by estimating values for the ring opening equilibria (i.e. ca. zero for $\Delta \bar{V}(K_1)$ and $\Delta \bar{V}(K_2)$), the following results were arrived at: for the cobalt(III) complex $\Delta V^{\neq}(k_1) = \Delta V^{\neq}(k_2) = 3 \pm 3$ $cm^3 mol^{-1}$, while for the chromium(III) and rhodium(III) complexes $\Delta V^{\neq}(k_2) = \Delta V^{\neq}(k_3) = -18 \pm 3$ $cm^3 mol^{-1}$. The latter are reconcilable with an associative attack of a water molecule or hydronium ion on the protonated, "ring-opened" form of the complex. The cobalt reaction appears to be basically dissociative in character leading to positive activation volumes. It has been shown that rate-determining loss of an oxalate ligand is accompanied by a redox process yielding $C_2O_2^-$ or CO_2^- radicals and reduction to cobalt(II) [117].

The pressure dependence of the rate of the acid-catalyzed aquation of a second oxalate ligand has been studied, namely from *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$, as well as the analogous reaction of *cis*-$Cr(CH_2C_2O_4)(OH_2)_2^-$ (where $CH_2C_2O_4^{2-}$ = malonate dianion) [118]. Small volumes of activation were found: 1.7 ± 0.7 $cm^3 mol^{-1}$ for *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ at 45°C in 3 M $HClO_4$ and 2.4 ± 0.6 $cm^3 mol^{-1}$ at 65°C in 0.5 M $HClO_4$ ($\mu = 1$ M) for *cis*-$Cr(CH_2C_2O_4)_2(OH_2)_2^-$. The reaction sequence is believed to take the form [119]

$$cis\text{-}Cr(aa)_2(OH_2)_2^- + H_3O^+ \overset{K}{\rightleftharpoons} Cr(aa)(aaH)(OH_2)_3 \tag{19}$$

$$\mathrm{Cr(aa)(aaH)(OH_2)_3 + H_3O^+ \xrightarrow{k} Cr(aa)(OH_2)_4^+ + HaaH} \qquad (20)$$

where aa represents the unprotonated ligand. According to the authors' opinion dissociation of the single protonated ligand in eqn. (20), or the associative attack of a water molecule, as the rate-determining process should give rise to negative $\Delta V^{\neq}_{\mathrm{exp}}$ values [118]. The former would lead to an increase in electrostriction while the latter derives from the negative $\Delta V^{\neq}_{\mathrm{intr}}$ associated with bond formation. The measured $\Delta V^{\neq}_{\mathrm{exp}}$ values are not in agreement with these mechanisms, but their similarity indicates that a common mechanism prevails. The authors [118] estimated a value of <2 cm^3 mol^{-1} for eqn. (19) so that $\Delta V^{\neq}$ for eqn. (20) must be of the order of 3 cm^3 mol^{-1}, consistent with a mechanism involving direct protonation of the coordinated carboxylate followed by the dissociation of the fully protonated acid to form a five-coordinate intermediate. It is worth mentioning here that such a mechanism deviates from that proposed for the corresponding trisoxalato complex [119].

The aquation of tris(1,10-phenanthroline)iron(II) and its 5-nitro- and 4,7-dimethyl- derivatives was studied at 35°C and in 1 M H_2SO_4 up to ca. 1700 bar [120]. The activation volumes were reported at 15.4 ± 0.4, 17.9 ± 0.3 and 11.6 ± 0.6 cm^3 mol^{-1}, respectively, and were shown to be virtually independent of pressure. These values, together with the positive entropies of activation, provided strong support for a dissociative mechanism. The possibility of a step-wise breaking of the two Fe—N bonds incorporating a unidentate intermediate could be ruled out due to the severe steric restrictions imposed by the adjacent phen rings. Therefore, a simultaneous stretching of both Fe—N bonds was favored. By neglecting any contribution from either $\Delta V^{\neq}_{\mathrm{solv}}$ or any shortening of the remaining Fe—N bonds, the volume swept out by the leaving phen ligand could be calculated using the various bond distances and van der Waals radii available in the literature. On the basis of such calculations, the Fe—N bond extensions on forming the transition state were given at 61 (phen), 72 (5-NO_2—) and 45 pm (4,7-Me_2—) corresponding to a degree of bond breaking of 39, 46 and 28%, respectively. These estimates were taken to be more in keeping with an I_d mechanism. Specific interactions of the substituted phen ligands were considered not to contribute significantly to the differences in the $\Delta V^{\neq}_{\mathrm{exp}}$ values.

(iv) Anation reactions

For anation reactions, the leaving group is inherently neutral and consequently the dissociation of this ligand does not involve changes in electrostriction so that this type of reaction has similar characteristics to the solvent exchange reactions. Furthermore, being the reverse of aquation, they provide an opportunity to verify the mechanism assigned to aquation. Conversely, preassociation of the incoming nucleophile with the substrate often complicates the interpretation by introducing a preassociation equilibrium which must be accounted for with an appropriate volume term.

TABLE 9

Volumes of activation for the anation of $M(NH_3)_5OH_2^{3+}$ [121]

M	Y	T (°C)	$[H^+]$ (M)	μ (M)	$\Delta V^{\neq}_{\text{exp}}$ ($cm^3\ mol^{-1}$)
Co	Cl^-	60	0.1	2.0	1.4 ± 0.8
Co	SO_4^{2-}	60	0.1	2.0	2.3 ± 1.8
Rh	Cl^-	60	0.1	2.0	3.0 ± 0.7
Cr	NCS^-	50	0.1	1.0	−4.9 ± 0.6
Cr	NCS^-	50	0.1	0.3	−2.4 ± 1.3

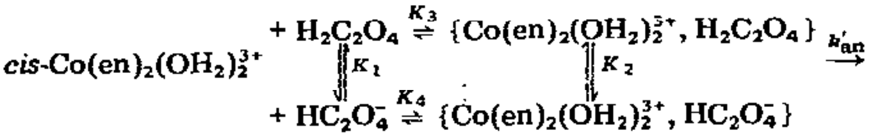
A recent study was made of the anation reactions of $M(NH_3)_5OH_2^{3+}$ [121] and these data are presented in Table 9. These reactions are generally believed to proceed according to an interchange mechanism represented by the equations

$$M(NH_3)_5OH_2^{3+} + X^{n-} \overset{K_{IP}}{\rightleftharpoons} \{M(NH_3)_5OH_2^{3+}, X^{n-}\} \tag{21}$$

$$\{M(NH_3)_5OH_2^{3+}, X^{n-}\} \xrightarrow{k} M(NH_3)_5X^{(3-n)+} + H_2O \tag{22}$$

Surprisingly, in each case K_{IP} was $< 0.3\ M^{-1}$, even for the doubly-charged nucleophile SO_4^{2-}. Nevertheless, by accepting the existence of an "ion pair" intermediate, $\Delta V^{\neq}_{\text{exp}}$ is then comprised of the volume changes incurred upon ion-pair formation and the actual interchange step in eqn. (22). For the ion pair $\{Co(NH_3)_6^{3+}, SO_4^{2-}\}$, $\Delta \overline{V}_{IP}$ is strongly temperature dependent, being 10.8 $cm^3\ mol^{-1}$ at 15°C and 4.5 $cm^3\ mol^{-1}$ at 40°C [122]. In addition, $\Delta \overline{V}_{IP}$ decreases with increasing ionic strength so that, under the experimental conditions of 60°C and $\mu = 2$ M, it was considered to represent only a small positive contribution to $\Delta V^{\neq}_{\text{exp}}$. Consequently, $\Delta V^{\neq}_{\text{solv}}$ was also assumed to be minimal due to the high ionic strength used and because the major effect of electrostriction, if any, should be observed during the formation of the contact ion pair. The $\Delta V^{\neq}_{\text{exp}}$ values in Table 9 were therefore attributed mainly to $\Delta V^{\neq}_{\text{intr}}$ for the interchange process. The similarity between the $\Delta V^{\neq}_{\text{exp}}$ values for the anation of $Co(NH_3)_5OH_2^{3+}$ by Cl^- and SO_4^{2-}, as well as for the corresponding water exchange reaction (e.g. $\Delta V^{\neq}_{\text{exp}} = 1.2\ cm^3\ mol^{-1}$ [80]). supported this proposition. Their positive signs and small values are in agreement with the dictates of an I_d mechanism. Conversely, the small negative $\Delta V^{\neq}_{\text{exp}}$ for the anation of $Cr(NH_3)_5OH_2^{3+}$ by NCS^- is in keeping with an I_a mechanism. The slightly larger $\Delta V^{\neq}_{\text{exp}}$ value at 0.3 M ionic strength was thought to reflect the increased positive contribution of $\Delta \overline{V}_{IP}$ at the lower ionic strength. The positive values of $\Delta V^{\neq}_{\text{exp}}$ for the anation of $Rh(NH_3)_5OH_2^{3+}$ by Cl^- conflicts with the assignment of an I_a mechanism to the water exchange reaction [81], but may be consistent with a general I mechanism proposed for the hydrolysis of $Rh(NH_3)_5NO_3^{2+}$ [99], or with an I_d mechanism [123].

The anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by oxalate involves a complex series of protonation equilibria incorporating both reactants [124,125]. However, by studying this system in specific pH regions, the overall reaction scheme could be simplified and volumes of activation assigned to individual reaction steps [125]. For example, in acidic medium ($[HNO_3] = 0.5$ M and $\mu = 2.0$ M ($NaNO_3$)) at 60°C the reaction scheme was reduced to



$$\begin{array}{lcl} & +\,H_2C_2O_4 \overset{K_3}{\rightleftharpoons} \{Co(en)_2(OH_2)_2^{3+}, H_2C_2O_4\} & \\ cis\text{-}Co(en)_2(OH_2)_2^{3+} & \Big\Updownarrow K_1 \qquad\qquad\qquad \Big\Updownarrow K_2 & \xrightarrow{k'_{an}} \\ & +\,HC_2O_4^- \overset{K_4}{\rightleftharpoons} \{Co(en)_2(OH_2)_2^{3+}, HC_2O_4^-\} & \end{array}$$

$$\text{“}Co(en)_2(OH_2)(C_2O_4)^{+}\text{”} \xrightarrow{\text{fast}} Co(en)_2C_2O_4^+ \qquad (23)$$

A pressure dependence of the observed rate constant at four oxalate concentrations (30°C and $\mu = 0.32$ M ($NaNO_3$)) yielded the values, $\Delta V^{\neq}_{an} = 4.8 \pm 0.2$ $cm^3\ mol^{-1}$ and $\Delta \overline{V}_{IP} = 2.3 \pm 0.6$ $cm^3\ mol^{-1}$ [125], where the latter was derived from $K_{IP} = (K_1K_4 + [H^+]K_3)/(K_1 + [H^+])$. Under the prevailing experimental conditions $[H^+] > K_1$ and $K_1K_4 > [H^+]K_3$, such that $\Delta\overline{V}_{IP} \simeq (\Delta\overline{V}_1 + \Delta\overline{V}_4)$. Given that $\Delta\overline{V}_1 = -12$ $cm^3\ mol^{-1}$, then $\Delta\overline{V}_4 \simeq 10$ $cm^3\ mol^{-1}$. However, van Eldik and Harris [126] have recently shown that the large ion pair association constants reported in this system [124,125] are not found in perchlorate media, suggesting that nitrate ion plays a specific role in these reactions.

A similar investigation in neutral medium [125] involved the equations

$$Co(en)_2(OH)OH_2^{2+} + C_2O_4^{2-} \overset{K_5}{\rightleftharpoons} (Co(en)_2(OH)OH_2^{2+}, C_2O_4^{2-}) \qquad (24)$$

$$(Co(en)_2(OH)OH_2^{2+}, C_2O_4^{2-}) \xrightarrow{k''_{an}} Co(en)_2(OH)C_2O_4 + H_2O \qquad (25)$$

and the rate equation

$$1/k''_{obs} = 1/k''_{an} + 1/(k''_{an} + K_5[C_2O_4^{2-}]) \qquad (26)$$

The values of k''_{an} and K_5 obtained from eqn. (26) were corrected for the presence of some diaquo-species and for the pressure dependence of the buffer used. The respective values of $\Delta V^{\neq''}_{an}$ and $\Delta\overline{V}_5$ are 4.6 ± 0.4 $cm^3\ mol^{-1}$ and a rather surprising negative value of -1.0 ± 1.5 $cm^3\ mol^{-1}$. A comparison of $\Delta V^{\neq''}_{an}$ and the virtually identical $\Delta V^{\neq'}_{an}$ with 5.9 ± 0.2 $cm^3\ mol^{-1}$ obtained for water exchange with *trans*-$Co(en)_2(OH_2)_2^{3+}$ [85] suggests that a common I_d mechanism is operative. Furthermore, virtually zero values for $\Delta\beta^{\neq}_0$ for all three reactions supported this postulate.

Additional evidence for a dissociative process was provided from a comparison of the water exchange rates with the rate of interchange within the "oxalate" ion pair. For example, the rate of water exchange in *cis*-$Co(en)_2(OH_2)_2^{3+}$ is four times faster than the rate of interchange within the ion pair, $\{Co(en)_2(OH_2)_2^{3+}, H_2C_2O_4\}$. The rate of water exchange in the more labile *cis*-$Co(en)_2(OH)OH_2^{2+}$ cation is twice the interchange rate, k''_{an}.

The final aspect of this research [125] dealt with the oxalate ring-closing reaction which, in the pH region 7—8, can be represented by the equations

$$\mathrm{Co(en)_2(OH)C_2O_4 + H^+ \overset{1/K_6}{\rightleftharpoons} Co(en)_2(OH_2)C_2O_4^+} \qquad (27)$$

$$\mathrm{Co(en)_2(OH_2)C_2O_4^+ \xrightarrow{k_{an}'''} Co(en)_2C_2O_4^+ + H_2O} \qquad (28)$$

After correcting the rate constants for pressure effects on the buffer and by assuming a $\Delta\bar{V}$ for the protonation equilibrium (27) of 2.3 $\mathrm{cm^3\ mol^{-1}}$, a $\Delta V_{an}^{\neq'''}$ of 0 ± 1.2 $\mathrm{cm^3\ mol^{-1}}$ was estimated (at 50°C and $\mu = 0.37$ M ($\mathrm{NaNO_3}$)). As a dissociative rate-determining loss of the $\mathrm{OH_2}$ ligand would lead to a positive $\Delta V_{an}^{\neq'''}$, this must be compensated by bonding of the free carboxalate to the cobalt center. An $\mathrm{I_a}$ mechanism was therefore favored for this process.

The step-wise anation of $\mathrm{Cr(OH_2)_6^{3+}}$ by oxalate was investigated at pH = 2.7 where only the aquo form of the complex is present and oxalate exists mainly as $\mathrm{HC_2O_4^-}$ [127]. The volumes of activation for the step-wise formation of $\mathrm{Cr(C_2O_4)_3^{3-}}$ are -2.2 ± 1.0, -8.2 ± 0.5 and -10.0 ± 0.5 $\mathrm{cm^3\ mol^{-1}}$ at 25°C and $\mu = 1$ M, respectively [127]. The negative signs of the first two values are compatible with a basically associative mechanism, as positive contributions stemming from electrostriction would be expected to diminish upon formation of the prerequisite ion pairs. This is clearly emphasized by a comparison of $\Delta V_{exp}^{\neq}$ for the water exchange with $\mathrm{Cr(OH_2)_6^{3+}}$, -9.3 ± 0.3 $\mathrm{cm^3\ mol^{-1}}$ [83], with that for the bioxalate anation of this species, viz. -2.2 ± 1.0 $\mathrm{cm^3\ mol^{-1}}$. Schenk and Kelm [127] demonstrated the role played by electrostriction by applying the Born equation [128] to this system. This equation predicts a positive $\Delta V_{solv}^{\neq}$ for the first step, a smaller value for the second and a negative value for the third, which are transposed on a constant negative $\Delta V_{intr}^{\neq}$ term stemming from bond formation.

For anation reactions proceeding via a limiting dissociative mechanism, the volumes of activation must be positive and independent of the incoming nucleophile for a given substrate. A good example of this behavior can be found in the anation of $\mathrm{Co(CN)_5OH_2^{2-}}$ by $\mathrm{Br^-}$, $\mathrm{I^-}$ and $\mathrm{NCS^-}$ where volumes of activation of 8.4 ± 1.0, 9.4 ± 1.6 and 8.2 ± 0.9 $\mathrm{cm^3\ mol^{-1}}$ (at 40°C and $\mu = 1$M), respectively, are recorded [112]. In other words, electrostriction is not a factor in these reactions and $\Delta V_{exp}^{\neq}$ directly reflects Co—$\mathrm{OH_2}$ bond stretching. Similarly, the anation of *cis*-$\mathrm{RhCl_4(OH_2)_2^-}$ and $\mathrm{RhCl_5OH_2^{2-}}$ at 20°C and $\mu = 4$ M resulted in activation volumes of 15.7 ± 6.5 and 14.7 ± 1.6 $\mathrm{cm^3\ mol^{-1}}$, respectively [115]. The difference in the average $\Delta V_{exp}^{\neq}$ for the latter two systems may be due to differences in the geometries of the respective intermediates, viz. trigonal-bipyramidal for the pentacyano reactions and tetragonal-pyramidal for the $\mathrm{RhCl_n(OH_2)_{6-n}^{(n-3)-}}$ system [115].

(v) Equilibration reactions

This section is devoted exclusively to results obtained from T-jump studies where it is not always possible to treat the hydrolysis and anation reactions within their equilibration individually.

In this category the most extensively studied system involves the formation reactions of Fe(III)—halide and —pseudohalide complexes according to the overall scheme [129—131]

$$\begin{tikzcd}
\mathrm{Fe}^{3+} + \mathrm{X}^- \arrow[r, shift left, "k'_1"] \arrow[d, shift left, "K_{\mathrm{OH}}"] & \mathrm{FeX}^{2+} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "K_{\mathrm{OHX}}"] \\
\mathrm{FeOH}^{2+} + \mathrm{X}^- \arrow[u, shift left] \arrow[r, shift left, "k'_2"] & \mathrm{Fe(OH)X}^{+} \arrow[l, shift left, "k_{-2}"] \arrow[u, shift left]
\end{tikzcd} \qquad (29)$$

By allowing for ion-pair formation, eqn. (29) expands to

$$\begin{tikzcd}
\mathrm{Fe}^{3+} + \mathrm{X}^- \arrow[r, shift left, "K_1"] \arrow[d, shift left, "K_{\mathrm{OH}}"] & \mathrm{Fe}^{3+},\mathrm{X}^- \arrow[l, shift left] \arrow[r, shift left, "k_1"] \arrow[d, shift left, "K_{\mathrm{OH,X}}"] & \mathrm{FeX}^{2+} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "K_{\mathrm{OHX}}"] \\
\mathrm{FeOH}^{2+} + \mathrm{X}^- \arrow[u, shift left] \arrow[r, shift left, "K_2"] & \mathrm{FeOH}^{2+},\mathrm{X}^- \arrow[l, shift left] \arrow[u, shift left] \arrow[r, shift left, "k_2"] & \mathrm{Fe(OH)X}^{+} \arrow[l, shift left, "k_{-2}"] \arrow[u, shift left]
\end{tikzcd} \qquad (30)$$

It is understood that the Fe(III) species in eqns. (29) and (30) refer to fully hydrated ions, e.g. $\mathrm{Fe}^{3+} = \mathrm{Fe(OH_2)}_6^{3+}$. The combined results of these investigations are presented in Table 10. From the schemes shown in eqns. (29) and (30), it can be seen that $k'_1 = K_1 k_1$ and thus $\Delta V^{\ddagger}_{\mathrm{exp}} = \Delta V^{\ddagger\prime}_1 = \Delta \overline{V}_1 + \Delta V^{\ddagger}_1$. The same applies to $\Delta V^{\ddagger\prime}_2$. In the cases where X = Cl and NCS, $\Delta \overline{V}_1$ was calculated from Hemmes equation (31) [132], which is based on the expression for outer-sphere complex formation developed by Eigen [133] and Fuoss [134]

$$\Delta \overline{V}_{\mathrm{os}} = RT\{(|z_+ z_-|\, e^2/a\epsilon kT)(\partial \ln \epsilon/\partial P)_T - \beta\} \qquad (31)$$

where z_+ and z_- are the charges on the two ions; a is the distance of closest approach; ϵ is the dielectric constant; k is the Boltzmann constant and β is the compressibility of solution. For X = Br, $\Delta \overline{V}_1$ was calculated by an iteration procedure. The negative values for $\Delta V^{\ddagger}_1$ were presented as direct evidence of an associative attack by X^- on the hydrated Fe^{3+} ion. On the other hand, anation of the monohydroxo-iron(III)-species is considered [129—131] to follow a dissociative mechanism as demonstrated by the positive activation volumes, $\Delta V^{\ddagger\prime}_2$. The effect of the charge on the substrate was given as a possible reason for the change in mechanism [129,130]; higher charge density on Fe^{3+} was thought to raise the activation energy for a dissociative process, thereby favoring an associative one. The assignment of an associative mechanism to the k_1 path conflicts with the mechanistic concept of Eigen [135] who proposed a dissociative mechanism for the interchange reactions of Fe(III).

Although the anation of Ni^{2+} is generally accepted as proceeding via an

TABLE 10

Volumes of activation ($cm^3 mol^{-1}$) for the reaction of Fe(III) with X^- at 25°C

Path	Cl^- [a]	Br^- [b]	NCS^- [c]
k'_1	−4.5 ± 1.1	−8 ± 4	ca. 0
k_2	7.8 ± 1.0		7.1 ± 1.0
k_{-1}	−9.2 ± 0.7	−2 ± 4	
$k_{-2}K_{OHX}$	2.2 ± 1.5	2 ± 2	
k_1	−9.9	−19 ± 4	−1.2
K_{OH} [d]		1.6 ± 0.1	3.0 ± 0.5
K_1 [d]		11 ± 1	8.9 ± 0.5

[a] Taken from ref. 129, μ = 1.5 M. [b] Taken from ref. 130, μ = 2.0 M. [c] Taken from ref. 131, μ = 0.2 M. [d] Measured independently.

encounter or ion-pair intermediate, the parameters for the overall reaction k_f and k_b (eqn. (32)) are usually reported

$$Ni^{2+} + L^{n-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NiL^{(2-n)+} \qquad (32)$$

A variety of such reactions has been investigated and the volumes of activation are listed in Table 11. The positive values for $\Delta V_f^{\neq}$ reinforce the theory of Eigen [135] that bond stretching in the transition state predominates. Using eqn. (31), Grant [136] derived a value for $\Delta \overline{V}_{os}$ of 3 $cm^3 mol^{-1}$ for ion-pair formation between Ni^{2+} and glycinate, while Jost [39] obtained a value of 3.5 $cm^3 mol^{-1}$ for Ni^{2+} and murexide by the same method. In both cases the activation volume for interchange within the ion-pair remained positive, thereby underlining the dissociative character of the mechanism.

Grant and Wilson [139] suggested that for bidentate ligands, ring closure could be rate determining. Therefore, they studied the reaction of the neutral ligand PADA with a series of nickel complexes, NiL, where L = ethylenediaminediacetate (EDDA), nitrilotriacetate (NTA), diethylenetriamine

TABLE 11

Volumes of activation and the total volume change for the formation of Ni^{2+} complexes

Ligand	$\Delta V_f^{\neq}$ ($cm^3 mol^{-1}$)	$\Delta \overline{V}$ ($cm^3 mol^{-1}$)	T (°C)	Ref.
Glycine	10.0 ± 1.0	2.1 ± 0.6	25	136
Murexide	12.2 ± 1.5	22.6 ± 1.5	25	39
Imidazole	11.0 ± 1.6		28	137
PADA [a]	7.7 ± 0.3	0.9 ± 0.7	49	138
NH_3	9.2 ± 0.3	−2.3 ± 0.7	30	138

[a] PADA = pyridine-2-azo-dimethylaniline.

TABLE 12

Volumes of activation and the total volume change for the reaction of PADA with $\mathrm{NiL}^{(2-n)+}$, at 25°C, $\mu = 0.3$ M and pH = 7 [a]

L^{n-}	$\Delta V_f^{\neq}$ ($\mathrm{cm^3\ mol^{-1}}$)	$\Delta V_b^{\neq}$ ($\mathrm{cm^3\ mol^{-1}}$)	$\Delta \overline{V}$ ($\mathrm{cm^3\ mol^{-1}}$)
EDDA	6.9 ± 0.4		
NTA	6.9 ± 0.4	7.0 ± 0.4	−0.1 ± 0.8
dien	4.2 ± 0.3	3.6 ± 0.3	0.6 ± 0.5
trien	2.6 ± 0.4	5.9 ± 0.2	−3.2 ± 0.6
tren [b]	2.9 ± 0.3	5.2 ± 0.3	−2.4 ± 0.5

[a] Taken from ref. 139. [b] Measured at 20°C.

(dien), triethylaminetetramine (trien) and 2,2′,2″-triaminotriethylamine (tren). The relevant volume parameters are given in Table 12. The $\Delta V_f^{\neq}$ values could be divided into two groups [139], $\mathrm{Ni(OH_2)_6^{2+}}$, Ni(EDDA) and $\mathrm{Ni(NTA)^-}$ with larger values (5 to 8 $\mathrm{cm^3\ mol^{-1}}$), and $\mathrm{Ni(trien)^{2+}}$ and $\mathrm{Ni(tren)^{2+}}$ having smaller values of ca. 3 $\mathrm{cm^3\ mol^{-1}}$. The value for $\mathrm{Ni(dien)^{2+}}$ of 4 $\mathrm{cm^3\ mol^{-1}}$ lies between those of the two groups. The authors [139] used two methods to estimate the rate constant for dissociation of the monodentate PADA ligand and found good agreement for all complexes except $\mathrm{Ni(trien)^{2+}}$ and $\mathrm{Ni(tren)^{2+}}$ They concluded that $\mathrm{Ni(OH_2)_6^{2+}}$, Ni(EDDA) and $\mathrm{Ni(NTA)^-}$ react with a rate-determining dissociation of a water molecule, whereas ring closure is rate determining for the reactions on $\mathrm{Ni(trien)^{2+}}$ and $\mathrm{Ni(tren)^{2+}}$, while $\mathrm{Ni(dien)^{2+}}$ was thought to belong to an intermediate class.

Stranks [17] pointed out that there is a complete lack of any apparent correlation between $\Delta V^{\neq}$ and $\Delta \overline{V}$ for these reactions, as can be clearly seen from the data listed in Tables 11 and 12. Grant and Wilson [139] proposed that this may be due to a delicately balanced interplay of the significance of the metal characteristics, the ligand and the solvent in these reactions.

For various reasons it seems to be appropriate to include the reactions of $\mathrm{Zn^{2+}}$ and $\mathrm{Cu^{2+}}$ next to those of $\mathrm{Co^{2+}}$ at this stage. The reactions of these metal ions in glycerol were conducted under conditions where only 1 : 1 metal—PADA complexes were observed [140]. The rate constants, including that of $\mathrm{Ni^{2+}}$, were virtually the same, whereas they differ by a factor of 10^4 in water and are 10^2 to 10^3 times larger than the values calculated for diffusion controlled reactions. However, relaxation times for the $\mathrm{Ni^{2+}}$ and $\mathrm{Cu^{2+}}$ reactions were too long to allow accurate rate constants to be determined and therefore pressure and temperature dependence studies were only possible for $\mathrm{Co^{2+}}$ and $\mathrm{Zn^{2+}}$. The respective volumes of activation for formation are 9.6 ± 0.5 and 12.2 ± 0.8 $\mathrm{cm^3\ mol^{-1}}$ at 20°C [140]. The volume of activation for a diffusion controlled process, $\Delta V^{\neq}_{\mathrm{diff}}$, was calculated according to the equation (η = viscosity)

$$\Delta V^{\neq}_{\mathrm{diff}} = -RT(\mathrm{d}\ln k_{\mathrm{diff}}/\mathrm{d}P)_T = RT(\mathrm{d}\ln \eta/\mathrm{d}P)_T \qquad (33)$$

For glycerol, values of $\Delta V^{\neq}_{\mathrm{diff}}$ were determined to be 15.5 $\mathrm{cm^3\ mol^{-1}}$ at 30°C and 12.5 $\mathrm{cm^3\ mol^{-1}}$ at 75°C. The value of $\Delta V^{\neq}_{f}$ for Zn^{2+} is in reasonable agreement with $\Delta V^{\neq}_{\mathrm{diff}}$ while the corresponding value for Co^{2+} is significantly smaller (noting that $\Delta V^{\neq}_{f}$ for Co^{2+} at 43°C is only 7.6 ± 0.4 $\mathrm{cm^3\ mol^{-1}}$ [140]). Therefore, the reaction of Zn^{2+} with PADA appears diffusion controlled, despite the low rate constant, whereas the same reaction involving Co^{2+} is chemically activated, as well as being partially diffusion controlled.

(vi) Ligand substitution reactions

Six kinetic criteria by which one can establish the existence of a dissociative, D, mechanism for substitution reactions were recently outlined [141]. These included a new criterion which stated that $\Delta V^{\neq}_{\mathrm{exp}}$ should be positive and independent of the incoming nucleophile when the leaving group is uncharged. The authors went on to propose that the rate-determining dissociation may be represented by

$$ML_5X \rightleftharpoons \{ML_5\cdots X\}^{\neq} \rightleftharpoons \text{Products} \qquad (34)$$

The partial molar volume of the substrate was considered to be equivalent to the sum of the partial molar volumes of the ML_5 moiety and the ligand X. The volume of the transition state is made up of two similar contributions and an addition term $V(\delta X^{\neq})$, which is the volume swept out as the M—X bond is stretched. Using assumptions discussed earlier [17,96], it was accepted that $\bar{V}(ML_5) = \bar{V}(ML_5^{\neq})$ and $\bar{V}(X) = \bar{V}(X^{\neq})$. Consequently, $\Delta V^{\neq}_{\mathrm{exp}} = V(\delta X^{\neq}) = A_x\,\Delta l$, where A_x is the effective cross-sectional area of X and Δl is the extent to which the M—X bond is stretched in the transition state. The observed volumes of activation are shown in Table 13. These values comply with the "sixth" criterion in that they are positive and independent of the entering group. Thus, for the substrate $Fe(CN)_5(3,5\text{-}Me_2py)^{3-}$, a mean value of $\Delta V^{\neq}_{\mathrm{exp}}$ of 20.7 $\mathrm{cm^3\ mol^{-1}}$ can be assigned. The insensitivity of the rate constant for the dissociative step to the composition of various mixed aqueous solvents [142] indicates that changes in solvation of the leaving 3,5-Me_2py

TABLE 13

Volumes of activation for the substitution of pentacyanoferrate(II) at 25°C and μ = 0.5 M [141]

Reactants		$\Delta V^{\neq}_{\mathrm{exp}}$ [a] ($\mathrm{cm^3\ mol^{-1}}$)
$Fe(CN)_5(3,5\text{-}Me_2py)^{3-}$	+ CN^-	20.5 ± 0.8
	+ pyrazine	21.2 ± 1.0
	+ imidazol	20.3 ± 1.0
$Fe(CN)_5(3\text{-}CNpy)^{3-}$	+ CN^-	20.6 ± 0.5

[a] Calculated according to eqn. (1).

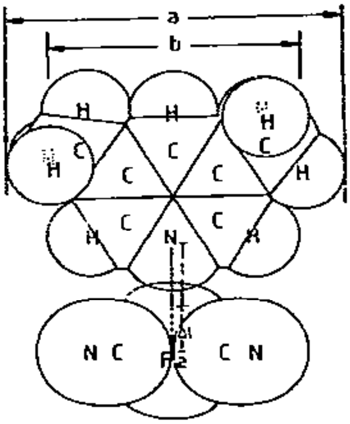


Fig. 5. The activated complex in the dissociative reaction of $Fe(CN)_5(3,5\text{-}Me_2py)^{3-}$ taken from ref. 141: where l = 195 pm = ground state Fe—N distance; Δl = Fe—N bond extension = 139 pm; a = 910 pm and b = 670 pm (c = 370 pm = the thickness of the 3,5-Me_2py ring).

ligand are of little significance in this step. As a result, $\Delta V^{\neq}_{\text{exp}}$ was attributed entirely to the volume swept out by the leaving group. A scaled diagram showing the relevant dimensions is shown in Fig. 5. No net volume change was anticipated from movement of the substituent methyl groups, so that $\Delta V^{\neq}_{\text{exp}} = 10^{-30}\, N_A \times b \times c \times \Delta l = 20.7$ with the result that $\Delta l = 139$ pm. Complete cleavage of the Fe—N bond, which has a length of 197 pm in the ground state, would correspond to the sum of the respective van der Waals radii, or 355 pm. The authors then calculated that the Fe—N bond is elongated in the transition state to 139/158 or ca. 88% of the distance corresponding to complete dissociation. By substituting a for b in the calculation of Δl, the percentage bond extension amounted to 65%, but in neither case was this considered to be sufficient as to allow a water molecule to approach the Fe center close enough to form a bond. In other words, these results also supported the assignment of a D mechanism. By applying this procedure to the unsymmetrical ligand 3-CNpy, 70% was calculated for the percentage bond separation in $Fe(CN)_5(3\text{-}CNpy)^{3-}$.

Finally, positive entropies of activation were found and attributed to solvent interaction effects. It is also very significant that these authors [141] also state that extra rotational modes of solvent molecules in close proximity to $Fe(CN)_5^{3-}$ and the heterocyclic moiety would result in positive contributions to $\Delta S^{\neq}$, but that no corresponding contribution to $\Delta V^{\neq}_{\text{exp}}$ exists.

The pressure dependence of the nucleophile-dependent rate constants for substitution by CN^- and OH^- into $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ was recently reported [143]. It must be mentioned that the hydroxide dependence does not involve conjugate-base catalysis so that these results may be treated within the concept of a normal substitution process. The volumes of activation and the entropies of activation, shown in parentheses, are as follows: $Fe(phen)_3^{2+}$, with CN^- 19.8 ± 1.0 (4 ± 20) and with OH^-, 19.7 ± 0.3 (18 ± 3); $Fe(bpy)_3^{2+}$, with CN^-, 20.9 ± 1.6 (37 ± 9 J K^{-1} mol^{-1}) and with OH^-, 21.5 ± 0.4 cm^3 mol^{-1} [143]. The reactions with CN^- were followed at 25°C, whereas those with OH^- were studied at 20°C. In keeping with the generalized criterion for a D mechanism [141], large positive $\Delta V^{\neq}_{\text{exp}}$ values were found and they are independent of the nature of the leaving group. They are also similar for both substrates and closely resemble the values obtained for the aquation of these species, viz. 15.4 ± 0.4 cm^3 mol^{-1} for $Fe(phen)_3^{2+}$ [120] and 11.7 ± 0.7 cm^3 mol^{-1} for $Fe(bpy)_3^{2+}$ [144]. The dissociative process was thought to involve the simultaneous stretching of both Fe—N bonds on the rigid phen and bpy ligands. A consecutive mechanism involving a one-ended dissociation of the phen ligand could be ruled out due to steric restrictions imposed by the other two phen ligands. The consistency of the $\Delta V^{\neq}_{\text{exp}}$ values, as opposed to the $\Delta S^{\neq}$ values, again underscored the proposal that many solvent rearrangements are only reflected in $\Delta S^{\neq}$ and the relationship between these two parameters as claimed by Twigg [105] is unjustified in many cases.

For the substitution reactions of metal carbonyls, two types of kinetic behavior have been observed. A first-order reaction, generally associated with a positive $\Delta S^{\neq}$, and second-order processes with negative entropies of activation. These were explained in terms of variations in mechanism, namely, dissociative and associative, respectively. The volumes of activation are listed in Table 14 for a number of these reactions [145]. The positive activation volumes were interpreted in terms of a dissociative mechanism as electrostriction can be ignored in these systems involving neutral molecules. This assignment concurs with the observed reaction order, i.e. the rate constants are independent of the nucleophile concentration. Brower and Chen [145] also used the positive $\Delta V^{\neq}_{\text{exp}}$ values to calculate M—C bond extensions which proved to be 170 and 250 pm for $Mo(CO)_6$ and $Cr(CO)_6$, respectively, and 140 pm for $Ni(CO)_4$. The approximate value for complete bond rupture was given as 235 pm, demonstrating that bond stretching is very advanced in the transition state.

TABLE 14

Volumes of activation for the substitution reactions of metal carbonyls [145]

Reactants	Kinetic order	Solvent	T (°C)	$\Delta V^{\neq}_{\text{exp}}$ (cm^3 mol^{-1})
$Mo(CO)_6 + Ph_3P$	First	"Isooctane"	103.0	10 ± 1
$Cr(CO)_6 + Ph_3P$	First	Cyclohexane	124.0	15 ± 1
$W(CO)_6 + Bu_3P$	Second	Cyclohexane	120.0	—10 ± 2
$Cr(CO)_6 + N_3^-$	Second	Acetone	24.0	0 ± 1
$Ni(CO)_4$ [a] + $(EtO)_3P$	First	Heptane	0.0	8 ± 1

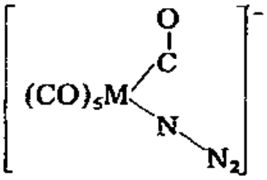
[a] For convenience the four-coordinated Ni compound is included here.

The "neutral displacement" reaction of $W(CO)_6$ was considered to be associative in character due to its second-order property and this harmonizes with the negative $\Delta V^{\neq}_{exp}$.

The reaction of $Cr(CO)_6$ with N_3^- is unusual and takes the following form

$$Cr(CO)_6 + N_3^- \rightarrow Cr(CO)_5NCO^- + N_2 \quad (35)$$

with a transition state of the structure



The observed $\Delta V^{\neq}_{exp}$ of 0 $cm^3\ mol^{-1}$ indicates that both bond making and breaking are important in the transition state because the expected values for the limiting cases are —10 and +10 $cm^3\ mol^{-1}$, respectively.

(vii) Isomerization reactions

This section is divided into three parts in order to deal separately with the various types of rearrangements, namely geometric and linkage isomerizations as well as racemization reactions. These types of reactions and their pressure dependencies were recently reviewed by Lawrance and Stranks [18].

The volume of activation for the isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ to the *cis* isomer is markedly pressure dependent [103]. These data are shown in Table 15. Here again electrostriction changes are minimal so that the large positive $\Delta V^{\neq}_{exp}$ values provide direct evidence of a dissociative mechanism. In this case the $\Delta\beta^{\neq}$ values are even more significant to the elucidation of the intimate reaction mechanism. For the isomerization in 0.05 M $HClO_4$, the transfer of a water molecule from the coordination sphere to the first hydration sphere, as dictated by an I_d mechanism, should result in a compressibility coefficient of $(\beta_{hydr.\ sphere} - \beta_{coord.\ sphere}) << 0.06\ cm^3\ mol^{-1}\ kbar^{-1}$, i.e. virtually zero. However for a D mechanism, the limiting value of $\Delta\beta^{\neq}$

TABLE 15

Volume parameters for the *trans*—*cis* isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ [103]

Electrolyte	T (°C)	$\Delta V^{\neq}_{exp}$ ($cm^3\ mol^{-1}$)	$\Delta\beta^{\neq}$ ($cm^3\ mol^{-1}\ kbar^{-1}$)
0.05 M, $HClO_4$	34.5	14.3 ± 0.2	0.9 ± 0.2
0.05 M, $HClO_4$	46.0	14.2 ± 0.2	1.0 ± 0.2
0.5 M, $HClO_4$	48.0	14.2 ± 0.5	8 ± 2
1 M, $HClO_4$	45.0	12.6 ± 0.8	10 ± 3
1 M, $NaClO_4$	45.0	13.7 ± 0.7	10 ± 3
1 M, $HClO_4$	50.5	13.7 ± 0.5	11 ± 3

should be $(\beta_{\text{bulkwater}} - \beta_{\text{coord. sphere}}) = (0.84 - 0.06) \cong 0.8$ cm^3 mol^{-1} kbar^{-1}, which closely resembles the experimental value in 0.05 M acid. In more concentrated electrolyte media, a considerable amount of solvent is expected to be bound in ionic aggregates. In order to adjust to the dissociating ligand and the moving ethylenediamine rings, partial disordering of the hydrated ionic aggregates is necessary, thereby releasing a number of electrostricted water molecules into the more compressible bulk solvent. This explanation accounts for the large $\Delta\beta^{\neq}$ values found in 1 M electrolyte solutions.

Therefore, water exchange and isomerization must proceed through different transition states. The former probably involves a tetragonal-pyramidal intermediate [85], while isomerization occurs through a trigonal-bipyramidal intermediate [103].

The *trans* to *cis* isomerization of *trans*-Co(en)$_2$(CH$_3$COO)OH$_2^{2+}$ was studied at three different solution compositions: 0.05 M (HClO$_4$); 0.05 M (HClO$_4$), $\mu = 1.0$ M (NaClO$_4$); and 1.0 M (HClO$_4$); at 45.2°C [146]. The respective volumes of activation under these conditions are 7.9 ± 0.3, 6.5 ± 0.4 and 5.6 ± 0.6 cm^3 mol^{-1}. These relatively small positive values, coupled with the fact that $\Delta\beta^{\neq} = 0$ cm^3 mol^{-1} kbar^{-1}, lead to the conclusion that an I$_d$ mechanism should be assigned to this reaction and that the leaving group is the neutral water molecule. Other possible mechanisms such as the dissociative release of CH$_3$COO$^-$, which is likely to result in a negative $\Delta V^{\neq}_{\text{exp}}$, or a twist mechanism, which should exhibit a near-zero $\Delta V^{\neq}_{\text{exp}}$, could be ruled out. In particular, a comparison of these parameters with those for the isomerization of *trans*-Co(en)$_2$(OH$_2$)$_2^{3+}$ strongly supports the mechanistic assignment made here [146].

The mechanism for the *trans* to *cis* isomerization of *trans*-Cr(C$_2$O$_4$)$_2$(OH$_2$)$_2^-$ is very different from those discussed above. This is immediately apparent from the volumes of activation which are: −16 ± 1 cm^3 mol^{-1} in water, water/methanol, and water/dioxane mixtures; −9.8 ± 1 cm^3 mol^{-1} in aqueous solutions of Ca(NO$_3$)$_2$; and −5.4 ± 1.0 cm^3 mol^{-1} in the presence of HClO$_4$ [147]. The former value was confirmed in a more recent study from which a $\Delta V^{\neq}_{\text{exp}}$ value was found of −16.6 ± 0.5 cm^3 mol^{-1} and a $\Delta\beta^{\neq}$ value of −1.8 ± 0.6 cm^3 mol^{-1} kbar^{-1} at pH = 3.15 and a temperature of 30°C [118]. Although these results could be explained by an associative attack of a water molecule on the Cr(III) center, the rate of exchange of an aquo ligand is known to be 150 times slower than the rate of isomerization [148], which therefore eliminates this mechanism from contention. However, the complete kinetic data are consistent with a rate-determining opening of an oxalate ring. The catalytic effect of protons and cations originates from direct interaction with the coordinated carboxylate, thereby weakening the Cr—O bond. This interaction quenches the charge, which develops on the carboxate ion during one-ended ring opening, and is reflected in the less negative $\Delta V^{\neq}_{\text{exp}}$ values found in the presence of HClO$_4$ and Ca(NO$_3$)$_2$. In other words, the increase in electrostriction around the free end of the monodentate oxalate ligand is mainly responsible for the large negative $\Delta V^{\neq}_{exp}$ values. Stranks and co-workers [118] estimated this contribution to be ca. -12.5 cm^3 mol^{-1}. Furthermore, the entropy of activation is negative, -61 J K^{-1} mol^{-1} [118, 147], in keeping with strong electrostrictive effects.

The transfer of a single water molecule from the bulk solvent to the region of a carboxylate anion was estimated to result in a change in the compressibility coefficient of -0.74 cm^3 mol^{-1} kbar^{-1} [118]. As $\Delta\beta^{\neq} = -1.8$ cm^3 mol^{-1} kbar^{-1}, two water molecules were thought to enter the hydration sheath surrounding the carboxylate anion in the transition state.

In contrast to the behavior of the oxalato complex, *trans*-$Cr(CH_2C_2O_4)_2(OH_2)_2^-$ undergoes isomerization at a much slower rate (ca. 300 times) and exhibits a $\Delta V^{\neq}_{exp}$ of 8.9 ± 0.3 cm^3 mol^{-1} at 65°C (pH = 3.00, $\mu = 1$ M) and a $\Delta S^{\neq}$ of 74 ± 5 J K^{-1} mol^{-1} [118]. A basically dissociative mechanism was therefore favored in this case and because of the lack of any detectable pressure dependence of $\Delta V^{\neq}_{exp}$, as well as the somewhat smaller $\Delta V^{\neq}_{exp}$ (cf. +15 cm^3 mol^{-1} for complete dissociation of a water molecule), the intimate mechanism was considered to be I_d in character.

The analogous reactions of *trans*-$Co(en)_2(SeO_3)OH_2^+$ and *trans*-$Co(en)_2(SeO_3H)OH_2^{2+}$ yielded volumes of activation, which were virtually pressure independent, of 7.6 ± 0.7 (15°C) and 8.0 ± 0.6 (25°C) cm^3 mol^{-1}, respectively [17]. These values are very similar to the volume of activation observed for the malonato complex and may be rationalized in terms of an I_d mechanism.

The linkage isomerization reactions of the complexes, $M(NH_3)_5ONO^{2+}$, where M = Co(III), Rh(III) or Ir(III), were investigated in aqueous solution ($\mu = 0.1$ M) [149]. Previous studies [150,151] had shown that the nitrito ligand isomerizes completely to the nitro form and that, at least in the case of the cobalt complex, no significant exchange between coordinated and free nitrite ions takes place within the time scale of the isomerization. The volumes of activation for all three complexes were found to be very similar (i.e. -6.7 ± 0.4 cm^3 mol^{-1} for M = Co(III) and 30°C; -7.4 ± 0.4 cm^3 mol^{-1} for M = Rh(III) and 20°C; and -5.9 ± 0.6 cm^3 mol^{-1} for M = Ir(III) and 30°C) supporting the idea of a common intramolecular rearrangement of the nitrito ligand.

An alternative approach is to apply eqn. (12) to the data for $Co(NH_3)_5ONO^{2+}$ to test whether the volume data also comply with the condition for a dissociative mechanism. Using the value for $\overline{V}\{Co(NH_3)_5^{3+}\}$ of 55.1 cm^3 mol^{-1} [96], as discussed earlier, and the partial molar volumes of the $Co(NH_3)_5ONO^{2+}$ cation and NO_2^- anion of 82.3 and 30.9 cm^3 mol^{-1}, respectively, a calculated $\Delta V^{\neq}$ emerges of +3.7 cm^3 mol^{-1} which is substantially different from the experimentally obtained value. Finally, the partial molar volume of the final product was determined to be 69.4 cm^3 mol^{-1} so that $\Delta\overline{V} = -12.9 \pm 1.5$ cm^3 mol^{-1}. The transition state therefore lies half-way between the initial and final states with partial bonding of the N and O atoms to the cobalt.

It is of interest to note that negative volume changes were also observed for the linkage isomerization of $Ni(1,4\text{-}Et_2en)_2(ONO)_2$ and $Ni(1,4\text{-}Me_2en)_2\cdot(ONO)_2$ in chloroform [152], i.e. $\Delta\overline{V} = -7.2 \pm 1.0$ and -4.5 ± 0.8 cm^3 mol^{-1}, respectively.

The linkage isomerization of the thiocyanato ligand in $Co(NH_3)_5SCN^{2+}$ was also shown to be an intramolecular process based on the results of an ^{15}NCS exchange study [153]. The volume of activation for this isomerization was measured at -5.3 ± 0.8 cm^3 mol^{-1} at 50°C and $\mu = 0.1$ M [154]. Application of eqn. (12) to this system yielded a calculated value for $\Delta V^{\neq}$ of 2.7 ± 1.8 cm^3 mol^{-1} from which it could also be concluded that a dissociative mechanism does not prevail here. The overall volume change was given as -0.5 ± 1.7 cm^3 mol^{-1}. Thus it appears that Co—N bond formation is well advanced in the transition state. The $\Delta V^{\neq}_{exp}$ value is definitely not in agreement with a mechanism which involves Co—SCN bond cleavage and the formation of an "intimate ion pair" in the transition state, as this would lead to a positive $\Delta V^{\neq}_{exp}$ value. In DMSO the volume of activation under the same experimental conditions is -1.0 ± 1.2 cm^3 mol^{-1} showing that solvation effects are of importance in these reactions, possibly due to some degree of charge separation in the transition state [154].

Lawrance and Suvachittanont [155] have tabulated the existing volumes and entropies of activation for the racemization and isomerization reactions of a range of octahedral complexes. They established that a qualitative relationship appears to exist between these two parameters (similar to the relationship proposed earlier by Twigg [105] for acid hydrolysis reactions) except for those reactions where a twist mechanism is operative. This relationship is recreated in Fig. 6 where it can be seen that points 4—7 fall well outside the line. The remaining reactions are considered to be either dissociative or associative in character.

The individual racemization reactions will now be treated in detail. Firstly the racemization reactions of the symmetrical tris(1,10-phenanthroline)iron(II) and -nickel(II) complexes can be considered. The appropriate volumes of activation are given in Table 16 [18,156]. The close agreement between the $\Delta V^{\neq}_{exp}$ values for racemization and aquation of $Fe(phen)_3^{2+}$ implies a common reaction mechanism. However, the former proceeds nine times more rapidly than aquation and this does not support the common mechanism proposal. It has already been argued that the aquation reaction is a dissociative process [120] in which simultaneous stretching of the two Fe—N bonds occurs. This mechanism can be equally well assumed for racemization. Within this concept Lawrance and Stranks [156] discussed the effects which arise upon excitation of low spin d^6 iron(II), $^1A_1$, to a high spin transition state, $^5T_2$, particularly with respect to the associated volume changes. An expansion of the metal—ligand bond lengths is the result [157—159]. An example was quoted for the spin equilibria of bis(2-(2-pyridylamino)-4-(2-pyridyl)thiazole)iron(II) chloride in aqueous solution where $\Delta\overline{V} = 11$ cm^3 mol^{-1} [159]. Positive contributions of this order of magnitude also allow a twist mechanism to be considered. A small positive $\Delta V^{\neq}_{exp}$ is normally associated with this intramolecular process,

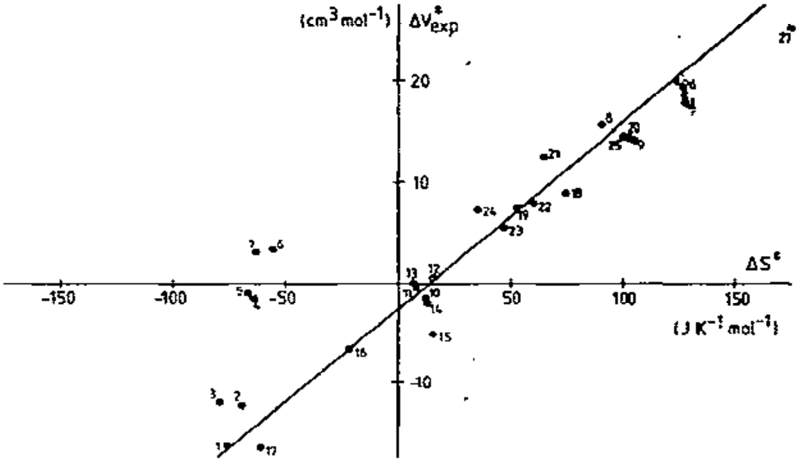


Fig. 6. $\Delta V^{\ne}_{\text{exp}}$ versus $\Delta S^{\ne}$ for racemization and geometric isomerization of octahedral complexes [155]. Key: 1, $Cr(ox)_3^{3-}$; 2, $Cr(ox)_2phen^-$; 3, $Cr(ox)_2bpy^-$; 4, $Cr(ox)(phen)_2^+$; 5, $Cr(ox)(bpy)_2^+$; 6, $Cr(phen)_3^{3+}$; 7, $Cr(bpy)_3^{3+}$; 8, $Fe(phen)_3^{2+}$; 9, $Fe(phen)_3^{2+}$; 10, $Ni(phen)_3^{2+}$; 11, $Ni(phen)_3^{2+}$; 12, $Ni(phen)_2bpy^{2+}$; 13, $Ni(phen)_2bpy^{2+}$; 14, $Ni(phen)(bpy)_2^{2+}$; 15, $Ni(phen)(bpy)_2^{2+}$; 16, $Co(Ph_2dtc)_3$; 17, *trans*-$Cr(ox)_2(OH_2)_2^-$; 18, *trans*-$Cr(mal)_2(OH_2)_2^-$; 19, *trans*-$Co(en)_2(SeO_3H)OH_2^{2+}$; 20, *trans*-$Co(en)_2(OH_2)_2^{3+}$; 21, *trans*-$Co(en)_2(OH_2)_2^{3+}$; 22, *trans*-$Co(en)_2(acet)OH_2^{2+}$; 23, *trans*-$Co(en)_2(acet)OH_2^{2+}$; 24, *trans*-$Co(en)_2(SeO_3)OH_2^+$; 25, *trans*-$Co(en)_2(OH)OH_2^{2+}$; 26, β-$Co(EDDA)tn^+$; 27, β-$Co(EDDA)en^+$.

but due to the dominance of the spin-change factor, a value of ca. 5 cm^3 mol^{-1} is, in this case, consistent with this mechanism. The agreement between the volumes of activation for aquation and racemization would then have to be purely coincidental. No definite conclusion could be reached [156] in favor of either mechanism.

For the $Ni(phen)_3^{2+}$ cation, the rates of aquation, racemization and phenanthroline exchange are similar, inferring a common dissociative mechanism. The volumes of activation shown in Table 16 substantiate this idea. The small negative values for $\Delta V^{\ne}_{\text{exp}}$ could arise from a simultaneous contraction of the remaining four Ni—N bonds during the dissociation of one phen ligand. A square-planar low spin transition state would account for such a contraction, i.e. the reverse situation to that mentioned for the iron(II) analogue.

Although it bears little relation to their behavior in solution, *l*-$Fe(phen)_3^{2+}$, *l*-$Ni(phen)_3^{2+}$ and *d*-$Ni(phen)_3^{2+}$ all racemize in the solid state and exhibit volumes of activation of -0.9 ± 0.1, -1.1 ± 0.2 and -1.1 ± 0.1 cm^3 mol^{-1} (24—27°C), respectively [160]. A limiting dissociative mechanism was rejected, but an exact description of the reaction intermediate could not be made. It is noteworthy that the volumes of activation are the same for both optical isomers of the nickel complex.

High pressure investigations of the racemization of mixed phenanthroline,

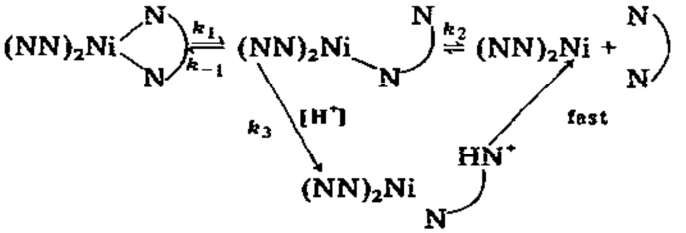
TABLE 16

Volumes and entropies of activation for the racemization of $Fe(phen)_3^{2+}$ and $Ni(phen)_3^{2+}$ [156]

Reactant	[HCl] (M)	$\Delta S^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)	$\Delta V^{\neq}_{exp}$ ($cm^3\ mol^{-1}$)
$Fe(phen)_3^{2+}$	0.01	104 ± 10	14.2 ± 0.3
	1.0	89 ± 8	15.6 ± 0.3
	1.0 [a]	117 ± 8 [a,b]	15.4 ± 0.3 [a,c]
$Ni(phen)_3^{2+}$	0.01	8 ± 5	−0.4 ± 0.2
	1.0	12 ± 3	−1.5 ± 0.3
	1.0 [a]	3 ± 6 [a]	−1.2 ± 0.2 [a]

[a] These data refer to the aquation reaction. [b] Taken from ref. 157. [c] Taken from ref. 120.

bipyridyl and oxalato complexes of nickel(II) and chromium(III) have also been made by Stranks and co-workers [161,162]. The volumes of activation for the racemization and aquation of the nickel(II) cations are compared in Table 17. The more flexible and less sterically crowding bipyridyl ligands are capable of one-ended dissociation, whereupon ring closure leads to racemization while cleavage of the second Ni—N bond results in aquation. This mechanism is outlined in eqn. (36)



(36)

and accounts for the [H⁺] dependence of the observed rate constant. At high

TABLE 17

Activation volumes and entropies for the racemization and aquation of $Ni(phen)_2bpy^{2+}$ and $Ni(phen)(bpy)_2^{2+}$ at 20°C [161]

Reactant	[HCl] (M)	$\Delta S^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)	$\Delta V^{\neq}_{exp}$ ($cm^3\ mol^{-1}$)
$Ni(phen)_2bpy^{2+}$	0.01	16	0.6 ± 0.2
	1.0	7	−0.1 ± 0.05
	1.0 [a]	12 [a]	0.0 ± 0.5 [a]
$Ni(phen)(bpy)_2^{2+}$	0.01	18	−1.9 ± 0.2
	1.0	16	−5.2 ± 0.5

[a] These data refer to the aquation reaction.

$[H^+]$, k_1 is the single rate-determining step. Rotation of one bipyridine ring about the C(2)—C(2′) bond by 90° stretches the Ni—N bond by over 50%. In this conformation the complex was calculated to have virtually the same volume as the starting material with the result that $\Delta V^{\neq}_{exp}$ is approximately zero. The $\Delta V^{\neq}_{exp}$ values in 1 M acid are directly comparable and reflect differences in the degree of increased solvation during the activation process. The results at 0.01 M $[H^+]$ are composite values stemming from a number of rate constants. The similarity between the data in Tables 16 and 17 is therefore considered to be fortuitous and not the result of a common mechanism.

Strong evidence for a one-ended dissociative mechanism for the racemization of $Cr(ox)_3^{3-}$ was provided by $^{18}OH_2$ exchange studies [163]. The 12 oxygen atoms in $Cr(ox)_3^{3-}$ were found to be equivalent and in 1 M $HClO_4$ their total exchange rate is 11 times slower than the rate of racemization. In other words, racemization occurs through a rapid ring-opening and -closing process. This was also assumed from studies of the much slower aquation reaction (see eqns. (14)—(18)). In addition, both protons and metal ions accelerate racemization, reminiscent of the ring-opening mechanism for the isomerization of *trans*-$Cr(ox)_2(OH_2)_2^-$ [118,147]. In this connection it is interesting to note that the volumes of activation for the isomerization reaction (—16 $cm^3\ mol^{-1}$ [118,147]) and for the racemization of $Cr(ox)_3^{3-}$, given in Table 18, are virtually identical. Another common aspect of these two reactions is that the vacated coordination site in the transition state is not expected to be occupied by a water molecule. From a comparison of the volume changes for the dissociation of carboxylic acids and by allowing for the volume increase associated with Cr—O bond fission, viz. 1 $cm^3\ mol^{-1}$, Lawrance and Stranks [162] calculated a value for $\Delta V^{\neq}$ of —10 $cm^3\ mol^{-1}$. An additional negative contribution to $\Delta V^{\neq}$ was expected to arise from increased solvation of the five-coordinate intermediate.

The latter contribution should be dependent on the charge carried by the

TABLE 18

Volumes of activation for the racemization of chromium(III) complexes in 0.05 M HCl [162]

Reactant	T (°C)	$\Delta S^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)	$\Delta V^{\neq}_{exp}$ ($cm^3\ mol^{-1}$)
$Cr(ox)_3^{3-}$	15.0	-76 ± 4	-16.3 ± 0.2
$Cr(ox)_2(phen)^-$	25.0	-69 ± 2	-12.3 ± 0.15
$Cr(ox)_2(bpy)^-$	25.0	-79 ± 3	-12.0 ± 0.15
$Cr(ox)(phen)_2^+$	45.0	-64 ± 2	-1.5 ± 0.1
$Cr(ox)(bpy)_2^+$	45.0	-68 ± 2	-1.0 ± 0.05
$Cr(phen)_3^{3+}$	75.0	-56 ± 3	3.3 ± 0.05
$Cr(bpy)_3^{3+}$	75.0	-63 ± 3	3.4 ± 0.1

substrate. Consequently, assuming $Cr(phen)(ox)_2^-$ and $Cr(bpy)(ox)_2^-$ racemize by the one-ended dissociation of an oxalate ligand, a $\Delta V^{\neq}_{exp}$ value closer to -10 cm^3 mol^{-1} would be expected. As can be seen in Table 18, the $\Delta V^{\neq}_{exp}$ values are identical within experimental error and close to the calculated value. As both complexes also exchange all eight oxygen atoms at virtually identical rates [163], it is quite evident that the mechanism for racemization is dissociative, analogous to that for $Cr(ox)_3^{3-}$.

At the other extreme, $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$ both exhibit identical, positive activation volumes which are fully consistent with a twist mechanism. Some extension of the Cr—N bonds is anticipated during this process, as manifested in the slightly positive $\Delta V^{\neq}_{exp}$ values. Alternatively, these values may originate from the effect of squeezing out water trapped in the V-shaped pockets between the propeller blade-like chelate rings. The intramolecular twist mechanism is also characterized by slow rates of racemization due to relatively high activation enthalpies.

By comparison, the small $\Delta V^{\neq}_{exp}$ values for $Cr(phen)_2ox^+$ and $Cr(bpy)_2ox^+$ may be also taken as evidence for an intramolecular twist mechanism. The larger gaps between the chelate rings in these two examples do not require that water be squeezed out during the twist action, thereby removing the small positive contribution to $\Delta V^{\neq}_{exp}$.

(viii) Base hydrolysis reactions

The original high pressure kinetic investigation of an inorganic reaction dealt with the hydrolysis of $Co(NH_3)_5Br^{2+}$ in basic solution [16]. At that time, the mechanism was considered to be a simple first-order attack of hydroxide ion on the substrate and the $\Delta V^{\neq}_{exp}$ value of 8.5 cm^3 mol^{-1} (30°C, $\mu = 0.0004$ M) was discussed accordingly. Now it is generally accepted that base hydrolysis proceeds by a conjugate base (CB) mechanism of the type D_{CB}. Therefore, k_{obs} and $\Delta V^{\neq}_{exp}$ are composite quantities. The reaction sequence for the pentaammine complexes is as follows

$$M(NH_3)_5X^{3-n} + OH^- \xrightarrow{K} M(NH_3)_4NH_2X^{2-n} + H_2O \tag{37}$$

$$M(NH_3)_4NH_2X^{2-n} \xrightarrow{k} M(NH_3)_4NH_2^{2+} + X^{n-} \tag{38}$$

$$M(NH_3)_4NH_2^{2+} + H_2O \xrightarrow{\text{fast}} M(NH_3)_5OH^{2+} \tag{39}$$

Four more reactions of cobalt(III) pentammine complexes have been investigated, namely, X = SO_4, $\Delta V^{\neq}_{exp} = 19.5 \pm 1.1$ cm^3 mol^{-1} (15°C, $\mu = 0.5$ M) [17]; X = SeO_3, $\Delta V^{\neq}_{exp} = -17.1 \pm 1.0$ cm^3 mol^{-1} (25°C, $\mu = 0.5$ M) [17]; X = PO_4, $\Delta V^{\neq}_{exp} = 28.9 \pm 2.2$ cm^3 mol^{-1} (55°C, $\mu = 0.5$ M) [17]; X = Cl, $\Delta V^{\neq}_{exp} = 33.4$ cm^3 mol^{-1} (35°C, $\mu = 0.061$ M) [164]. With the exception of X = Br, the plots of ln k_{obs} against pressure are strongly curved, suggesting that a large number of water molecules are released from the solvation sphere [17]. However, for

X = SeO_3 ^{18}O studies indicate that Se—O bond breaking occurs, rather than Co—O bond cleavage, with the result that a large increase in solvation takes place in eqn. (38) [17]. This also accounts for the large negative $\Delta V^{\neq}_{exp}$ value as well as the negative $\Delta\beta^{\neq}$ value. Stranks [17] assigned a value of +18 cm^3 mol^{-1} to $\Delta\overline{V}$ for eqn. (37) so that for X = Br, the actual $\Delta V^{\neq}$ value is ca. —10 cm^3 mol^{-1} which is in reasonable agreement with $\Delta V^{\neq}_{exp}$ for the aquation of $Co(NH_3)_5Br^{2+}$, viz. —8.7 cm^3 mol^{-1} [36]. However, for the remaining complexes, $\Delta V^{\neq}$ is positive and although characteristic of a dissociative step, is nevertheless difficult to explain. Kitamura [164] calculated a value of 22.0 cm^3 mol^{-1} for the pre-equilibrium volume change. Thus for X = Cl, $\Delta V^{\neq}$ = 11.4 cm^3 mol^{-1} which was thought to be mainly due to the greater solvation and smaller intrinsic size of $Co(NH_3)_4NH_2^{2+}$ compared to $Co(NH_3)_4(NH_2)Cl^+$ [164].

Balt [165] used known partial molar volumes [96] to substitute in the equation

$$\Delta V^{\neq}_{exp} = \overline{V}(Co(NH_3)_4NH_2^{2+}) + \overline{V}^{\neq}_X + \overline{V}(H_2O) - \overline{V}(Co(NH_3)_5X) - \overline{V}(OH) \quad (40)$$

where $\overline{V}^{\neq}_X$ is the volume change introduced by bringing X into the first solvation sphere from the coordination sphere. It was also assumed that $\overline{V}(Co(NH_3)_4NH_2^{2+}) = \overline{V}(Co(NH_3)_6^{3+})$ = 55 cm^3 mol^{-1} [96]. Values for $\overline{V}^{\neq}_X$ of 31.0 for X = Br, 46.7 for X = Cl, and 43.5 for X = SO_4 were then derived from eqn. (40). The values for Cl and SO_4 are virtually twice the partial molar volumes of the free anions. Balt concluded that the leaving ligand must be in the first solvation sphere in the transition state where it has a larger volume than in bulk water. In other words, reaction (38) is an interchange process. A recent nucleophile competition study by Reynolds and Hafezi [166] for a series of base hydrolysis reactions of $Co(NH_3)_5X^{3-n}$ complexes also led to this conclusion.

The base hydrolysis of $Rh(NH_3)_5X^{2+}$ cations, where X = Cl, Br, I and NO_3, have also been studied as a function of pressure [99]. The pertinent data are given in Table 19. Equation (40) was adapted to this system with one variation which was to equate $\overline{V}^{\neq}_X$ and $\overline{V}(X)$. Using the corresponding assumption that $\overline{V}(Rh(NH_3)_4NH_2^{2+} = \overline{V}(Rh(NH_3)_6^{3+})$ = 63.2 ± 0.9 cm^3 mol^{-1}, values for

TABLE 19

Volume data (cm^3 mol^{-1}) for the kinetics of the base hydrolysis of $Rh(NH_3)_5X^{2+}$ at 40°C and μ = 1 M [99]

X	$\Delta V^{\neq}_{exp}$	$\overline{V}(Rh(NH_3)_5X^{2+})$	$\overline{V}(X)$
Cl	18.7 ± 0.7	82.3 ± 0.5	21.7_5
Br	20.2 ± 0.5	91.5 ± 1.6	29.4
I	20.4 ± 0.5	94.1 ± 0.3	41.0
NO_3	22.3 ± 0.9	93.2 ± 0.5	33.3

$\Delta V^{\neq}$ were calculated and, with the exception of X = I, found to be in good agreement with the experimentally obtained values listed in Table 19, viz. 20 ± 1 for X = Cl; 19 ± 3 for X = Br; 28 ±1 for X = I; and 21 ± 1 cm^3 mol^{-1} for X = NO_3. These results are, therefore, consistent with a D_{CB} mechanism, except for the reaction of the iodo complex. However, if the volume change resulting from the first step, namely eqn. (37), does involve ca. 21 cm^3 mol^{-1} [97], then this virtually accounts for the entire $\Delta V^{\neq}_{exp}$ values, which are surprisingly constant. This may indicate that the Rh—X bond is not completely broken in the transition state and that an I_d mechanism does, in fact, better describe this behavior. It must then be concluded that the small positive $\Delta V^{\neq}_{intr}$ is compensated by the increase in electrostriction due to charge development.

In their investigation of the base hydrolysis of $Cr(OH_2)_5I^{2+}$, Weekes and Swaddle [100] formulated the pre-equilibrium as a proton dissociation

$$(OH_2)_5CrI^{2+} \overset{K}{\rightarrow} (OH_2)_4Cr(OH)I^+ + H^+ \qquad (41)$$

and assigned a $\Delta \overline{V}$ of —2 cm^3 mol^{-1}, based on a comparison with other acid dissociations of aquo metal complexes. The observed $\Delta V^{\neq}_{exp}$ value is —1.6 ± 0.3 cm^3 mol^{-1} [100]. Thus, the actual activation volume for the dissociation of the conjugate base must be virtually zero, indicating that the effects of bond breaking and increased solvation effectively cancel each other. A D_{CB} mechanism was ascribed to this reaction. The greater acidity of aquo ligands over ammonia ligands could well support the assignment of eqn. (41) to this reaction, rather than an equation analogous to that favored earlier, viz. eqn. (37).

The rates of isomerization of β-Co(EDDA)(tn)$^+$ and β-Co(EDDA)(en)$^+$ to the α-isomers are first-order in [OH^-] [167]. The volumes of activation for these two reactions were found to be 19.9 (58.6°C) and 25.2 (63.6°C), respectively [167]. As these reactions were measured in a $NaHCO_3/Na_2CO_3$ buffer, the volumes of activation had to be corrected for the pressure dependence of the pH of the buffer system [168,169]. Corrected volumes of activation obtained in this manner amounted to 14.7 and 20.0 cm^3 mol^{-1}, respectively. The volume change accompanying the pre-equilibrium (analogous to eqn. (37)) was estimated to be 18.8 cm^3 mol^{-1} at 60°C, so that $\Delta V^{\neq}$ is equal to —4.1 cm^3 mol^{-1} for β-Co(EDDA)(tn)$^+$ and 1.2 cm^3 mol^{-1} for β-Co(EDDA)(en)$^+$. These values were considered consistent with the one-ended dissociation of the diamine ring according to a D_{CB} mechanism, with the positive $\Delta V^{\neq}$ for the ethylenediamine complex due to the greater Co—N bond strength for this ligand, i.e. $\Delta V^{\neq}_{intr}$ is more positive for the (en) complex than for the (tn) one.

(ix) Metal ion assisted hydrolysis reactions

The aquation of complexes containing halide or pseudohalide ligands is generally "catalyzed" by the presence of mercury(II) ions. The reaction sequence can also be broken down into a pre-association equilibrium followed by the rate-determining dissociation of the bridged intermediate. The sequence can be written as follows (using the example of the pentaammine complexes)

$$(NH_3)_5MX^{2+} + Hg^{2+} \xrightarrow{K} (NH_3)_5M\text{—}X\text{—}Hg^{4+} \tag{42}$$

$$(NH_3)_5M\text{—}X\text{—}Hg^{4+} \xrightarrow{k} (NH_3)_5M^{3+} + HgX^+ \tag{43}$$

$$(NH_3)_5M^{3+} + H_2O \xrightarrow{\text{fast}} (NH_3)_5MOH_2^{3+} \tag{44}$$

The volumes of activation for a series of pentaammine complexes have been determined (25°C, $[H^+] = 0.31$ M and $\mu = 0.6$ M) and are as follows [170]: -1.7 ± 1.0 for $Co(NH_3)_5Cl^{2+}$; 0.8 ± 0.5 for $Co(NH_3)_5Br^{2+}$; 0.7 ± 0.4 for $Cr(NH_3)_5Cl^{2+}$; and 1.0 ± 0.4 cm^3 mol^{-1} for $Rh(NH_3)_5Cl^{2+}$. As these results were obtained at mercury ion concentrations of ca. 0.09 M where the observed rate constant is a linear function of $[Hg^{2+}]$, it was not possible to separate the two volume contributions from eqns. (42) and (43) to $\Delta V^{\neq}_{\text{exp}}$. Nevertheless, the dominant contribution to $\Delta\overline{V}$ was considered to be the loss of a coordinated water from the Hg^{2+}(aq) ion. It was estimated that this would amount to ca. +14 cm^3 mol^{-1}, although negative volume effects stemming from increased solvent electrostriction and Hg—X bond formation would reduce this value somewhat to an effective $\Delta\overline{V}$ value of 8 cm^3 mol^{-1}. Consequently $\Delta V^{\neq}$ must equal -8 cm^3 mol^{-1} if the reasoning is valid.

The Hg^{2+} induced aquation of $Rh(NH_3)_5I^{2+}$ has the advantage of exhibiting a large K value (733 ± 56 M^{-1} at 11.7°C) so that the $\Delta\overline{V}$ value for this step and the $\Delta V^{\neq}$ value can be conveniently determined [171]. The following reaction parameters were obtained: $\Delta H = -16.7 \pm 1.3$ kJ mol^{-1}, $\Delta S = -5 \pm 3$ J K^{-1} mol^{-1}, $\Delta\overline{V} = -1.7 \pm 1.0$ cm^3 mol^{-1}; $\Delta H^{\neq} = 78 \pm 5$ kJ mol^{-1}, $\Delta S^{\neq} = -12 \pm 19$ J K^{-1} mol^{-1}, $\Delta V^{\neq} = 1.2 \pm 0.3$ cm^3 mol^{-1} at 11.7°C and $\mu = 0.3$ M [171].

Here again, $\Delta V^{\neq}_{\text{exp}}$ ($= \Delta\overline{V} + \Delta V^{\neq}$) is virtually zero. However, the two component values are quite different from those predicted above [170]. This may well indicate that the release of a water molecule from Hg^{2+}(aq) prior to, or concomitant with, the formation of the bridged species is not the dominant factor in determining the sign and magnitude of $\Delta\overline{V}$.

The volume changes associated with eqn. (43), assuming a D type mechanism, can be expressed in the following form:

$$\Delta V^{\neq}_{D} = \overline{V}(Rh(NH_3)_5^{3+}) + \overline{V}(HgI^+) - \overline{V}(Rh(NH_3)_5IHg^{4+}) \tag{45}$$

where

$$\overline{V}(Rh(NH_3)_5IHg^{4+}) = \Delta\overline{V} + \overline{V}(Rh(NH_3)_5X^{2+}) + \overline{V}(Hg^{2+}) - \overline{V}(H_2O) \tag{46}$$

Given that $\overline{V}(Rh(NH_3)_5^{3+}) = \overline{V}(Rh(NH_3)_\circ^{3+} = 63.2$ cm^3 mol^{-1} [96] and from the measured partial molar volumes of the participating ions, a $\Delta V^{\neq}_{D}$ of 52 ± 3 cm^3 mol^{-1} was calculated [171]. The enormous difference between this value and the observed $\Delta V^{\neq}$ value proves that a D mechanism does not operate in this system. This treatment was carried a step further by assuming that the maximum associative contribution to $\Delta V^{\neq}$, $\Delta V^{\neq}_{\mathrm{A}}$, would amount to —18 cm^3 mol^{-1}. Thus if n is the fraction of dissociative character which this reaction possesses, then $\Delta V^{\neq}$ is defined by

$$\Delta V^{\neq} = n\ \Delta V^{\neq}_{\mathrm{D}} + (1 + n)\ \Delta V^{\neq}_{\mathrm{A}} \tag{47}$$

A value for n of ca. 0.3 indicates that an interchange mechanism is more appropriate to this reaction. New evidence has been presented favoring an $\mathrm{I_d}$ mechanism to explain the product ratios resulting from the assisted aquation of two pentaamminecobalt(III) complexes [172].

A normal pressure investigation of the $\mathrm{Hg^{2+}}$ assisted aquation of *fac*-Rh-$\mathrm{(OH_2)_3Cl_3}$ established that the pre-association constant was relatively large, namely 137 M^{-1} at 20°C [173]. The unusually large equilibrium constant was considered to be the result of electrostatic interaction between the three "*cis*" chloride ligands and the $\mathrm{Hg^{2+}}$ ion, rather than to any specific covalent bonding. However, the equilibrium constant for *mer*-$\mathrm{Rh(OH_2)_3Cl_3}$ with $\mathrm{Hg^{2+}}$ is even larger (733 M^{-1} at 11.8°C) [171], which is difficult to reconcile with a purely electrostatic interaction. The results of a high pressure kinetic investigation of the latter reaction yielded the following parameters: $\Delta H = 6 \pm 2$ kJ mol^{-1}, $\Delta S = 76 \pm 7$ J K^{-1} mol^{-1}, $\Delta \overline{V} = 2.8 \pm 0.3$ cm^3 mol^{-1}; $\Delta H^{\neq} = 90 \pm 3$ kJ mol^{-1}, $\Delta S^{\neq} = 4 \pm 10$ J K^{-1} mol^{-1}, and $\Delta V^{\neq} = 8.1 \pm 0.4$ cm^3 mol^{-1} at 22.9°C and $\mu = 2$ M [171]. The slightly endothermic pre-equilibrium is in keeping with the weakness of the Hg—Cl bond in the bridged intermediate. In contrast to the formation of the Hg—I bridge, the negative contribution to $\Delta \overline{V}$ from Hg—Cl bond formation is small. In addition, electrostriction changes should also be less significant because the overall charge is "diluted" in the bridged intermediate in this case. The decomposition of the intermediate, involving Rh—Cl bond cleavage, must give rise to a positive $\Delta V^{\neq}_{\mathrm{intr}}$ which may be modified to some degree by small solvation changes.

The rate of aquation of $\mathrm{Co(NH_3)_5Br^{2+}}$ is accelerated by the presence of anionic polyelectrolytes in solution [174]. For example, in the presence of sodium polyethylenesulfonate, (PES) $\Delta G^{\neq} = 108$ kJ mol^{-1} ([NaPES] = 8×10^{-4} M), whereas in the absence of this electrolyte $\Delta G^{\neq} = 103.7$ kJ mol^{-1}. However the effect is much more apparent in the volumes of activation which decrease from 2.0 to —8.7 cm^3 mol^{-1} under these conditions. Desolvation of the reactant, and to a greater extent the transition state, was thought to be the underlying cause of this effect.

(x) *Oxidation—reduction reactions*

Outer-sphere electron transfer processes take place with the redox complex pair maintaining their coordination spheres intact. The volume effects anticipated for this reaction have been treated in considerable detail by Stranks [17]. He based his calculations on the Hush theory [175—177] and proposed eqn. (48) for the expected volume of activation, in direct analogy to the corresponding equation for the free energy of activation.

$$\Delta V^{\neq} = \Delta V^{\neq}_{\text{coul}} + \Delta V^{\neq}_{\text{SR}} + \Delta V^{\neq}_{\text{IR}} + \Delta V^{\neq}_{\text{DH}} \tag{48}$$

The respective components of this equation are derived from: the coulombic interaction as the two charged species approach each other; the associated solvent rearrangement around the charged transition state; the internal rearrangement of the metal—ligand bonds necessary for electron transfer; changes in the interionic interactions in a medium of finite ionic strength, estimated using the extended Debye—Hückel equation. Complex ions of charge 2+ and 3+, including their first coordination spheres, were considered to be virtually incompressible. The volumes of activation calculated in this manner are compared with the experimentally obtained values in Table 20.

The excellent agreement for the first two reactions attests to the validity of this approach. The thallic—thallous exchange [17,178] is somewhat more complicated in that it could proceed either by a simultaneous two electron transfer or by two successive one-electron steps. However, $\Delta V^{\neq}_{\text{calc}}$ for the former was predicted to be —25.2 cm^3 mol^{-1} at 30°C, in obvious disagreement with the measured value shown in Table 20. For the two-step mechanism, eqn. (48) had to be modified to allow for free energy and molar volume changes. The $\Delta V^{\neq}_{\text{calc}}$ value derived in this manner, shown in Table 20, is almost identical to $\Delta V^{\neq}_{\text{exp}}$, thereby establishing that thallium exchange involves a slow outer-sphere, one-electron transfer.

In less acidic medium, the ferric—ferrous exchange can be represented by

$$^*\text{Fe(OH}_2)_6^{3+} \overset{K_a}{\rightleftharpoons} {}^*\text{Fe(OH}_2)_5\text{OH}^{2+} + \text{H}^+ \tag{49}$$

$$^*\text{Fe(OH}_2)_5\text{OH}^{2+} + \text{Fe(OH}_2)_6^{2+} \xrightarrow{k} {}^*\text{Fe(OH}_2)_6^{2+} + \text{Fe(OH}_2)_5\text{OH}^{2+} \tag{50}$$

As shown in the previous sections, $\Delta V^{\neq}_{\text{exp}} = \Delta \overline{V}_a + \Delta V^{\neq}$. An independent spectrophotometric determination of K_a yielded a value for $\Delta \overline{V}_a$ of —1.2 ± 0.5 cm^3 mol^{-1} [17]. Thus with $\Delta V^{\neq}_{\text{exp}}$ = —0.4 ± 0.4 cm^3 mol^{-1} [17], $\Delta V^{\neq}$ must equal 0.8 ± 0.9 cm^3 mol^{-1}. For an outer-sphere mechanism, $\Delta V^{\neq}_{\text{calc}}$ was determined to be —11.4 cm^3 mol^{-1}. This provides strong support for an inner-sphere mechanism. The $\Delta V^{\neq}_{\text{exp}}$ for an inner-sphere mechanism is thought to be comprised of the same electrostatic, electrostrictive and ionic strength contributions as

TABLE 20

Volumes of activation for outer-sphere electron transfer reactions [17]

Exchange Partner	T (°C)	$\Delta V^{\neq}_{\text{calc}}$ (cm^3 mol^{-1})	$\Delta V^{\neq}_{\text{exp}}$ (cm^3 mol^{-1})
$\text{Co(en)}_3^{3+}/\text{Co(en)}_3^{2+}$	65	—18.4	—19.8 ± 1.5
$\text{Fe(OH}_2)_6^{3+}/\text{Fe(OH}_2)_6^{2+}$	2	—14.4	—12.2 ± 1.5
$\text{Tl}^{3+}\text{(aq)}/\text{Tl}^{+}\text{(aq)}$	30	—13.7	—13.2 ± 1.0 [a]

[a] Taken from ref. 178.

for outer-sphere formation (viz. -11.4 cm^3 mol^{-1}), as well as a positive contribution (12.2 cm^3 mol^{-1}) stemming from the dissociation of an aquo ligand from $Fe(OH_2)_6^{2+}$ prior to the formation of the hydroxo bridge. A negative contribution to $\Delta V^{\neq}_{exp}$ from $HO{-}Fe(OH_2)_5^{2+}$ bond formation should also not be ignored.

A similar situation arises in the electron exchange between $Cr(OH_2)_5OH^{2+}$ and $Cr(OH_2)_6^{2+}$ for which a $\Delta V^{\neq}_{exp}$ of 4.2 ± 1.1 cm^3 mol^{-1} was measured [17], while a value of -11.6 cm^3 mol^{-1} was calculated for an outer-sphere mechanism.

Positive volumes of activation were also reported [179] for the net redox reactions of $Co(NH_3)_5X^{2+}$ with Fe^{2+}(aq); net redox implies that $\Delta \overline{G}$ for the overall reaction is not zero as was the case for the reactions discussed up to this point. The volumes of activation are: 11 cm^3 mol^{-1} for X = F at 25°C and in 0.1 M $HClO_4$; 8 cm^3 mol^{-1} for X = Cl and Br at 35°C and in 0.1 M $HClO_4$; and 14 cm^3 mol^{-1} for X = N_3 at 25°C and in 0.1 M $HClO_4$, 0.9 M $NaClO_4$ [179]. Stranks [17] predicted values of -10.6 to -12.8 cm^3 mol^{-1} for an outer sphere mechanism, so that the positive activation volumes are consistent with an inner-sphere mechanism involving a halide or pseudohalide bridged intermediate.

The chemistry of these particular reactions becomes more interesting in dipolar aprotic solvents such as DMSO and DMF [180—183]. For example, in DMSO the activation parameters, particularly $\Delta S^{\neq}$, for X = Cl and Br are substantially different from those in water, whereas the corresponding parameters for X = F are comparable [180]. This is despite the fact that an inner-sphere mechanism operates in both solvents. A very convincing explanation of this anomalous behavior was given [180—183], whereby, for the chloro and bromo systems in DMSO or DMF, the stereochemistry of the Fe^{2+} ion changes from an octahedral to a tetrahedral geometry during, or immediately following, the formation of the bridged intermediate. The reactions in water, and for the fluoro system in DMSO or DMF, on the other hand occur with retention of octahedral symmetry by the iron center. The alternative reaction routes are illustrated in the following equations.

$$Co(NH_3)_5X^{2+} + FeS_6^{2+} \overset{K}{\rightleftharpoons} (NH_3)_5Co^{III}{-}X{-}{}^{II}FeS_5^{4+} + S \tag{51}$$

$$(NH_3)_5Co^{III}{-}X{-}{}^{II}FeS_5^{4+} \xrightarrow{k} (NH_3)_5Co^{II}{-}X{-}{}^{III}FeS_5^{4+} \tag{52}$$

$$(NH_3)_5Co^{II}{-}X{-}{}^{III}FeS_5^{4+} \rightarrow \text{products} \tag{53}$$

or

$$Co(NH_3)_5X^{2+} + FeS_6^{2+} \overset{K}{\rightleftharpoons} (NH_3)_5Co^{III}{-}X{-}{}^{II}FeS_3^{4+} + 3\ S \tag{54}$$

$$(NH_3)_5Co^{III}{-}X{-}{}^{II}FeS_3^{4+} \xrightarrow{k} (NH_3)_5Co^{II}{-}X{-}{}^{III}FeS_3^{4+} \tag{55}$$

$$(NH_3)_5Co^{II}{-}X{-}{}^{III}FeS_3^{4+} \rightarrow \text{products} \tag{56}$$

TABLE 21

Rate and activation parameters for the reduction of $Co(NH_3)_5X^{2+}$ by Fe^{2+} in H_2O and DMSO at 35°C

X	Solvent	$10^3 k_{obs}$ (M^{-1} s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}_{exp}$ (cm^3 mol^{-1})
F	H_2O [a]	7.6	56.0	−96	10.7 ± 0.1 [b]
Cl		1.6	60.6	−96	8.7 ± 0.3 [b,c]
Br		0.92	65.2	−84	6.4 ± 1.1 [b,c]
F	DMSO [d]	4730.	36.8	−108	10.3 ± 0.4 [e,c]
Cl		9.72	88.6	+12	3.8 ± 0.7 [e,c]
Br		2.51	90.7	+8	0.0 ± 0.4 [e,c]

[a] Ref. 185. [b] Recalculated from ref. 179. [c] 25°C. [d] Ref. 180. [e] Ref. 184

A high pressure study of this system in DMSO showed that $\Delta V^{\neq}_{exp}$ for X = F is in fact more positive than for either X = Cl or X = Br [184]. The volumes of activation [184], together with the enthalpies and entropies of activation for these reactions in DMSO [180] and water [185] are listed in Table 21. The positive entropies of activation for X = Cl and Br provide direct evidence in favor of reactions (54)—(56) [180]. On the other hand, the positive values of $\Delta V^{\neq}_{exp}$ can be interpreted in terms of eqns. (51)—(53) with the same variations in $\Delta V^{\neq}_{exp}$ being due to solvation effects and steric crowding at the bridging site [184].

As already mentioned, Watts and co-workers [182,183] reported that the same trends in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ exist in DMF and therefore proposed the same reaction mechanism "crossover" for X = Cl and Br as was suggested in DMSO. In the more recent paper [183], the parameters for the formation of the bridged intermediate, for which the equilibrium constant is quite larger (viz. 16 M^{-1} at 25°C), were separated from those of the rate-determining electron transfer step. The $\Delta S^{\neq}$ value for the latter is even more strongly positive, 57 ± 16 J K^{-1} mol^{-1}. Furthermore, the authors [183] quoted an as yet unpublished high pressure study of the reaction of $Co(NH_3)_5Cl^{2+}$ with Fe^{2+} in DMF. A $\Delta V^{\neq}_{exp}$ of 3.6 cm^3 mol^{-1} was given, which is identical to that shown in Table 21, and divided into a $\Delta \bar{V}$ of −4.1 cm^3 mol^{-1} and a $\Delta V^{\neq}$ of 7.7 cm^3 mol^{-1} for electron transfer. In this work, an alternative explanation of $\Delta V^{\neq}_{exp}$ was apparently given, whereby the release of three DMF molecules in eqn. (54) results in an increase in volume of 220 cm^3 mol^{-1}, which is compensated by a contraction of the $Fe(DMF)_6^{2+}$ as it rearranges to the $ClFe(DMF)_3$ moiety. This is an attractive rationalization of the volume data as it coincides with the "elegant" explanation of the $\Delta S^{\neq}$ variations.

Although the reaction of H_2O_2 with $VO_2(NTA)^{2-}$ strictly involves the insertion of H_2O_2 into the coordination sphere of vanadium(V) [186], it is a potential model reaction for redox processes. Using high pressure stopped-flow techniques, a pressure independent $\Delta V^{\neq}_{exp}$ of 3.3 ± 0.6 cm^3 mol^{-1} was derived

[186]. As solvation changes were thought to be negligible in this case, an associative mechanism was confirmed for this reaction.

C. REACTIONS OF SQUARE PLANAR COMPLEXES

(i) Substitution and isomerization reactions

The kinetics of substitution of d^8 square planar complexes are generally governed by a two-term rate equation

$$k_{\text{obs}} = k_1 + k_2[\text{Y}] \tag{57}$$

where Y represents the incoming nucleophile [76,77,187—189]. The accepted reaction scheme is

$$\text{ML}_3\text{X} + \text{S} \xrightarrow{k_1} \text{ML}_3\text{S} + \text{X} \tag{58}$$

$$\text{ML}_3\text{S} + \text{Y} \xrightarrow{\text{fast}} \text{ML}_3\text{Y} + \text{S} \tag{59}$$

$$\text{ML}_3\text{X} + \text{Y} \xrightarrow{k_2} \text{ML}_3\text{Y} + \text{X} \tag{60}$$

Gray and Olcott [190] quite elegantly demonstrated that the k_1-path involves the rate-determining entry of a solvent molecule (in their case the solvent was water) into the substrate, by scavenging the aquo intermediate complex with a minimum concentration of OH^- ions. Independent experiments [190,191] showed that the rates of anation of the solvent-containing species are indeed much faster than k_1 (greater by a factor of ca. 10^3), with the result that k_1 is independent of [Y]. The k_2-path is simply considered to result from the direct attack of Y on ML_3X to form a five-coordinate transition state. Consequently, k_2 varies dramatically with the nucleophilicity of Y. Both reaction sequencies are thought to involve an associative, A or I_a type, mechanism.

As virtually all the reactions of four-coordinate complexes proceed according to eqns. (58)—(60), in the following discussion each kinetic system will be treated individually, rather than subdividing them into separate classes of reaction, as was done for the octahedral complexes. We will attempt to demonstrate that the activation volume data are compatible with the mechanism outlined above and, in fact, further clarify this concept. However, a number of kinetic systems will be presented in which, due to internal factors such as steric crowding and/or the nature of the solvent, the mechanisms are controversial. Nevertheless, the $\Delta V^{\neq}_{\text{exp}}$ values provide strong support for a specific mechanism in each case.

The suitable choice of substrate, solvent, nucleophile and nucleophile concentration enables a number of systems to be studied by conventional high pressure techniques, spectrophotometric or conductometric, under conditions where $k_2[\text{Y}] >> k_1$.

TABLE 22

Second-order rate constants and activation parameters for the reaction of *trans*-Pt(py)$_2$(Cl)NO$_2$ with pyridine at 30°C [54]

Solvent	$10^3 k_2$ (M^{-1} s^{-1})	$\Delta H_2^{\neq}$ (kJ mol^{-1})	$\Delta S_2^{\neq}$ [a] (J K^{-1} mol^{-1})	$(\Delta V^{\neq}_{exp})_2$ [b] (cm^3 mol^{-1})
CH_3NO_2	7.38	55.6 ± 5.0	−75 ± 12	−6.2 ± 0.4 [c]
CH_3OH	7.35	49.3 ± 0.8	−94 ± 3	−8.8 ± 0.6 [d]
C_2H_5OH	8.18	51.8 ± 0.4	−88 ± 3	−13.1 ± 0.8 [d]
CH_2Cl_2	0.15	55.2 ± 3.8	−110 ± 10	−19.8 ± 1.7 [d]

[a] These values were calculated from the k_2 values in mole fraction units. [b] These values were corrected for the compressibility of the solvent. [c] At 10°C. [d] At 25°C.

The rates of substitution by pyridine (py) for chloride in the complex *trans*-Pt(py)$_2$(Cl)NO$_2$ were studied as a function of pressure in the solvents CH_3NO_2, CH_3OH, C_2H_5OH and CH_2Cl_2 [54]. The second-order rate constants and the corresponding activation parameters are shown in Table 22. The relatively low $\Delta H_2^{\neq}$ values and the strongly negative values of $\Delta S_2^{\neq}$ have commonly been taken as evidence for an associative mechanism. Furthermore, the insensitivity of $\Delta S_2^{\neq}$ to the nature of the solvent was thought to indicate that solvation changes are of minor importance in the activation of such complexes. The $(\Delta V^{\neq}_{exp})_2$ values, on the other hand, vary markedly with solvent. In other words, here is another example where $\Delta V^{\neq}_{exp}$ and $\Delta S^{\neq}$ do not exhibit parallel behavior.

Given a parameter which directly relates to $\Delta V^{\neq}_{solv}$, a plot of $(\Delta V^{\neq}_{exp})_2$ versus this variable should yield an intercept of $\Delta V^{\neq}_{intr}$, i.e. $\Delta V^{\neq}_{intr} + \Delta V^{\neq}_{solv} \simeq \Delta V^{\neq}_{intr} + f(\text{solvent})$. A parameter widely used in describing the solvent dependencies of $\Delta V^{\neq}_{exp}$ for a variety of organic reactions, in particular Menschutkin reactions [192], is derived from the pressure derivative of $\Delta G^{\neq}_{solv}$ in the Kirkwood equation [193] and is designated by q_p $(=(3/(2\epsilon + 1)^2)\,(d\epsilon/dP)_T$, where ϵ represents the dielectric constant of the solvent). The solvato-chromic E_T parameter is an empirical "solvent-describing" term. However, its pressure derivative, E_P, is only slightly solvent dependent [194] and therefore not suitable for this purpose. The linear relationship between $(\Delta V^{\neq}_{exp})_2$ and q_p for the abovementioned reaction is illustrated in Fig. 7. The intercept, $\Delta V^{\neq}_{intr}$, is equal to -4 ± 1 cm^3 mol^{-1} consistent with an associative process in which the Pt—py bond is only partially formed in the transition state. As no change in charge is involved in this step, the $\Delta V^{\neq}_{solv}$ contributions to $(\Delta V^{\neq}_{exp})_2$ (amounting to −2, −5, −9 and −16 cm^3 mol^{-1} for S = CH_3NO_2, CH_3OH, C_2H_5OH and CH_2Cl_2, respectively) appear to stem from a contraction of the solvent due to increased solvent interaction with the highly polar trigonal bipyramidal transition state. The dipole moment of *trans*-Pt(py)$_2$(Cl)NO$_2$ can only be expected to be 2 or 3 D, far less than that for the transition state of ca. 11 D, which was calculated from the slope of the line in Fig. 7 [54]. Moreover, the reac-

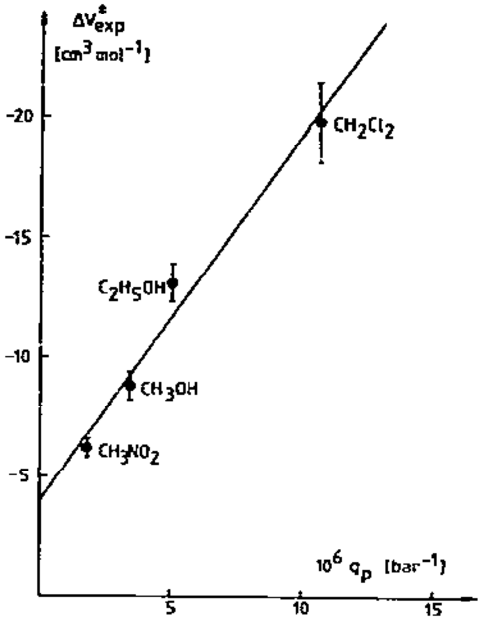


Fig. 7. The relationship between the volume of activation and the q_p parameter for the reaction of *trans*-Pt(py)$_2$(Cl)NO$_2$ with pyridine [54].

tion of pyridine with *cis*-Pt(py)$_2$(Cl)NO$_2$ and *trans*-Pt(PEt$_3$)$_2$Cl$_2$ in methanol at 30°C exhibited [54] $\Delta V^{\neq}_{\text{exp}}$ values of -5.5 ± 0.5 and -13.6 ± 0.8 cm^3 mol^{-1}, respectively. These substrates have dipole moments of ca. 10 D and zero, respectively, so that in methanol the corresponding $\Delta V^{\neq}_{\text{solv}}$ values are -2 and -10 cm^3 mol^{-1} (cf. -5 cm^3 mol^{-1} for $\Delta V^{\neq}_{\text{solv}}$ of *trans*-Pt(py)$_2$(Cl)NO$_2$). Thus the $\Delta V^{\neq}_{\text{solv}}$ term is mainly due to the change in dipole moment during the rate-determining step.

The volume of activation for the reaction of Br$^-$ with *trans*-Pt(PEt$_3$)$_2$Cl$_2$ in methanol was originally determined to be -27 ± 3 cm^3 mol^{-1} [195] (cf. -25.3 ± 1.0 cm^3 mol^{-1} [54]). It was assumed that $\Delta V^{\neq}_{\text{intr}}$ should be only slightly larger than -4 cm^3 mol^{-1}, so that the large $\Delta V^{\neq}_{\text{solv}}$ value must be due to an extremely polar transition state with the bulk of the negative charge residing on the newly-formed bromide ligand. In other words, this complies with the concept of a partially formed Pt—Br bond in the transition state and an overall A mechanism.

The substitution reactions of Pt(dien)X$^+$ (dien = diethylenetriamine) in water involve the complete two-term rate law, except for the reaction in alkaline solution where the observed rate constant is independent of [OH$^-$] [190]. In an earlier investigation of the reaction of Pt(dien)Br$^+$ with OH$^-$, $(\Delta V^{\neq}_{\text{exp}})_1$ was shown to be strongly pressure dependent, with a value at $P = 0$ of -18 ± 2 cm^3 mol^{-1} [196]. However, a recent comprehensive study of the hydrolysis reaction (k_1-path in eqn. (58)) under a variety of experimental conditions revealed $(\Delta V^{\neq}_{\text{exp}})_1$ to be essentially pressure insensitive up to ca. 1.8 kbar [197]. This study of the hydrolysis of Pt(dien)Cl$^+$ at 25°C and at various ionic strengths (10^{-2}—1 M), made up of different inert salts, also demonstrated that the magnitude of $(\Delta V^{\neq}_{\text{exp}})_1$ is virtually independent of the nature of the reaction medium or the leaving group. The values of $(\Delta V^{\neq}_{\text{exp}})_1$ ranged from −10.5 to −9.0 cm^3 mol^{-1} [197]. These results can only be interpreted in terms of an associative mechanism, preferably of the A type, although an I$_a$ mechanism could not be completely ruled out.

The effect of pressure on the hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ has also been studied and values of $(\Delta V^{\neq}_{\text{exp}})_1$ of −17 ± 2 and −14 ± 2 cm^3 mol^{-1}, respectively, were reported [198]. It was suggested that although the Pt—Cl bond remains virtually intact, two Pt—OH$_2$ bonds are formed in the transition state. These data did not allow any statement to be made as to the pressure dependence of $(\Delta V^{\neq}_{\text{exp}})_1$.

The $(\Delta V^{\neq}_{\text{exp}})_2$ values derived from the nucleophile dependent rate constants of the Pt(dien)X$^+$ substitution proved to be linear with pressure and provided direct evidence for an A mechanism. In this regard, the results listed in Table 23 establish that $(\Delta V^{\neq}_{\text{exp}})_2$ is independent of the leaving group by considering the three examples where azide is the entering ion, but is dependent on the nature of the entering ligand. $\Delta V^{\neq}_{\text{solv}}$ apparently plays a minor role because $(\Delta V^{\neq}_{\text{exp}})_2$ for Y = py is the same as for the charged nucleophile. In addition, as mentioned earlier (see the data in Table 2), the structured nature of water compared to other solvents, tends to minimize volume changes due to variations in solvation. The latter factor is probably more decisive and can be readily understood by considering the relatively low q_p value for water, viz. $<2 \times 10^{-6}$ bar^{-1}.

The $(\Delta V^{\neq}_{\text{exp}})_2$ values were also found to be smaller (more negative) than $\Delta\overline{V}$ for the overall volume change of the reaction [196], thereby establishing that the transition state is more compact than the products, i.e. the transition

TABLE 23

Volumes of activation for the substitution reactions of Pt(dien)X$^+$ with nucleophile Y in aqueous solution at 25°C and μ = 0.2 M [196]

X	Y	$(\Delta V^{\neq}_{\text{exp}})_2$ [a] (cm^3 mol^{-1})
Br$^-$	N_3^-	−8.5 ± 0.2
Br$^-$	py	−7.7 ± 0.5
Br$^-$	NO_2^-	−6.4 ± 0.7
Cl$^-$	N_3^-	−8.2 ± 1.3
I$^-$	N_3^-	−8.2 ± 0.7
N_3^-	I$^-$	−12.2 ± 0.1
N_3^-	SCN$^-$	−7.3 ± 0.1

[a] These values were corrected for the compressibility of the medium.

state most probably has a higher coordination number than the substrate.

A logical way of trying to force the d^8 complexes to change their mode of reaction to a more dissociative one is to try and prevent the solvent or nucleophile from reaching the metal center. This could possibly be accomplished by introducing bulky alkyl fragments into the amine groups of the dien ligand. Molecular models [199,200] show that these substituents lie above and below the plane of the complex in such a manner as to hinder the approach of a potential ligand. Indeed, k_1 for Pt(Et$_4$dien)Cl$^+$ (Et$_4$dien = 1,1,7,7-tetraethyldiethylenetriamine) in water is 8.5×10^{-6} s^{-1} at 80°C compared to 3.5×10^{-5} s^{-1} at 25°C for Pt(dien)Cl$^+$ [201], clearly illustrating the effect of steric hindrance. However, it does not necessarily imply that the reaction mechanism has changed. As the rate constants of such substituted dien Pt(II) complexes are too small to be conveniently measured, it is easier to look at the corresponding Pd(II) complexes, which are considerably more labile as can be seen from the data in Table 24. A strong trend in the k_1 values with increasing steric hindrance is also apparent for these Pd(II) reactions. Another very significant feature common to both systems is the dramatic decrease in k_2 down the series, particularly for the larger nucleophiles such as I$^-$. For instance, for the reaction of Pd(dien)Cl$^+$ with I$^-$, $k_2 = 2380 \pm 160$ M^{-1} s^{-1} at 15°C and μ = 0.05 M, whereas for the corresponding reaction with Pd(Et$_4$dien)Cl$^+$, $k_2 = (9.0 \pm 0.6) \times 10^{-4}$ M^{-1} s^{-1} [201,202].

The first-order rate constants and their activation parameters are listed in Table 25 for the k_1-path of the substitution reactions of Pd(Et$_4$dien)X^{n+} [205]. The trend in the rate constants indicates that some bond breaking apparently occurs during the formation of the transition state. Furthermore, this trend parallels the order of increasing Pd—X bond strength. The variation in k_1 originates from increases in $\Delta H_1^{\ddagger}$, although the relationship is irregular.

TABLE 24

First-order rate constants for the hydrolysis of Pd(R$_n$dien)Cl$^+$ complex ions in water at 15°C and μ = 0.05 M [201—204]

Substrate [a]	k_1 (s^{-1})
Pd(dien)Cl$^+$	19.2
Pd(Et$_3$dien)Cl$^+$	24.5
Pd(Me$_4$dien)Cl$^+$	0.135
Pd(Me$_5$dien)Cl$^+$	0.132
Pd(Et$_4$dien)Cl$^+$	0.00092
Pd(MeEt$_4$dien)Cl$^+$	0.00024
Pd(Et$_5$dien)Cl$^+$	0.00028

[a] Where Et$_3$dien = 1,4,7-triethyl-; Me$_4$dien = 1,1,7,7-tetramethyl-; Me$_5$dien = 1,1,4,7,7-pentamethyl-; MeEt$_4$dien = 4-methyl-1,1,7,7-tetraethyl-; Et$_5$dien = 1,1,4,7,7-pentaethyldiethylenetriamine.

TABLE 25

Summary of the rate data for the solvolysis of $Pd(Et_4dien)X^{n+}$ [a] in aqueous solution at 25°C [205]

X	$10^4 k_1$ (s^{-1})	$\Delta H_1^{\ne}$ ($kJ\ mol^{-1}$)	$\Delta S_1^{\ne}$ ($J\ K^{-1}\ mol^{-1}$)	$(\Delta V^{\ne}_{exp})_1$ ($cm^3\ mol^{-1}$)
Cl^-	21.6	65.5 ± 0.8	−74 ± 3	−14.9 ± 0.2
Br^-	17.4	65.6 ± 2.9	−75 ± 10	−13.3 ± 0.2
N_3^-	4.59	71.8 ± 0.8	−71 ± 2	−13.9 ± 0.5
I^-	2.65	71.4 ± 1.3	−69 ± 3	−11.5 ± 0.2
NCS^-	1.52	75.2 ± 1.7	−67 ± 6	−10.3 ± 0.2
NH_3	0.13	93.2 ± 2.3	−28 ± 7	−3.0 ± 0.9

[a] This complex was abbreviated as $Pd(teden)X^{n+}$ in ref. 205 to conform to IUPAC nomenclature.

The variation in $(\Delta V^{\ne}_{exp})_1$, on the other hand, plainly parallels the sequence in the k_1 values. However, on the basis of these results alone it is impossible to decide either the extent to which bond stretching is developed in the transition state, or whether the dissociative character of the reaction increases down the series. It is important to note that the scavenging technique used in the Pt(II) dien system [190] was applied to this system and showed that $Pd(Et_4dien)OH_2^{2+}$ is an intermediate in the hydrolysis step, thereby establishing that these reactions still possess substantial associative character. A kinetic study of this reaction in mixed aqueous solvents induced the authors [206] to favor an I_a mechanism for this path.

A plot of $(\Delta V^{\ne}_{exp})_1$ versus $\Delta \bar{V}_1$, which was obtained from the partial molar volumes of the products and reactants, yielded a straight line with a slope of ca. 0.5. As already discussed for the corresponding results of the aquation of $Cr(NH_3)_5X^{n+}$ complex ions [64], this may be taken as qualitative evidence for an I_a mechanism with approximately 50% bond stretching in the transition state. Analogous to the treatment of the $Cr(NH_3)_5X^{n+}$ system [96], this argument was pursued further [205] and the following volume equation was formulated from which the contribution to $(\Delta V^{\ne}_{exp})_1$ made by a 50% elongation of the Pd—X bond could be calculated.

$$(0.5\ \Delta V^{\ne}_{D}) = 0.5\{\bar{V}(Pd(Et_4dien)^{2+}) - \bar{V}(Pd(Et_4dien)X^{n+}) + \bar{V}(X^{n-2})\} \qquad (61)$$

The assumption was made that $\bar{V}(Pd(Et_4dien)^{2+}) \simeq \bar{V}(Pd(Et_4dien)NH_3^{2+})$. The volume quantities necessary to these calculations are shown in Table 26. Although no correlation could be found between $(0.5\ \Delta V^{\ne}_{D})$ and $(\Delta V^{\ne}_{exp})_1$, the values of $\Delta V^{\ne}_{A}$ (see last column in Table 26) obtained from $\Delta V^{\ne}_{A} = (\Delta V^{\ne}_{exp})_1 - (0.5\ \Delta V^{\ne}_{D})$ and assigned to the associative contribution to $(\Delta V^{\ne}_{exp})_1$, are surprisingly constant, with a mean value of −15.5 ± 0.9 $cm^3\ mol^{-1}$. Therefore, $\Delta V^{\ne}_{A}$ was attributed to the formation of a $Pd—OH_2$ bond, which naturally should be independent of X. These results represent quantitative proof for an I_a mechanism. The assumption which led to the value of $\bar{V}(Pd(Et_4dien)^{2+})$

TABLE 26

Summary of the volume data (cm^3 mol^{-1}) for the hydrolysis of Pd(Et$_4$dien)X^{n+} in aqueous solution at 25°C [205]

X	$\overline{V}$(Pd(Et$_4$dien)X^{n+})	$\overline{V}$(X^{n-2})	(0.5 $\Delta V^{\neq}_{\mathrm{D}}$)	$\Delta V^{\neq}_{\mathrm{A}}$
Cl^-	245.8	21.7$_5$	0.6	−15.5
Br^-	249.3	29.4	2.6	−15.9
N_3^-	252.6	31.8	2.2	−16.1
I^-	256.5	41.0	4.8	−16.3
NCS^-	258.1	40.2	3.6	−13.9
NH_3	225.1	24.8$_5$	12.5	−15.5

must be treated with some caution and although $\Delta V^{\neq}_{\mathrm{A}}$ remains equally constant if $\overline{V}$(Pd(Et$_4$dien)$^{2+}$) were assumed to be smaller than $\overline{V}$(Pd(Et$_4$dien)NH$_3^{2+}$), the distinction between an I$_a$ and an I$_d$ mechanism becomes less definite.

From the limited high pressure data available for the corresponding k_2-path [205], it was concluded that the mechanism must also be of the interchange type, but again it proved difficult to distinguish between I$_a$ and I$_d$.

The complex Pd(Et$_4$dien)SCN$^+$ isomerizes to the corresponding N-bonded thiocyanate complex in solution as well as in the solid state [207,208]. Steric crowding of the S-bonded ligand, arising from the size of the sulfur atom and, more importantly, the bent Pd—S—C bonds, were considered responsible for this phenomenon. The mechanism for isomerization was thought to be the same as that for solvolysis. Indeed, the rate constants and $\Delta H^{\neq}_1$ and $\Delta S^{\neq}_1$ values are identical for the two processes [207]. The volumes of activation for the isomerization and substitution (solvolysis path) by Br$^-$ in Pd(Et$_4$dien)SCN$^+$ in aqueous solution (μ = 0.1 M and 30°C) were also found to be identical within experimental error, viz. −10.8 ± 0.3 and −10.6 ± 0.4 cm^3 mol^{-1}, respectively [209]. For this "hydrolysis" reaction, application of eqn. (61) results in a value for $\Delta V^{\neq}_{\mathrm{A}}$ of −10 ± 2 cm^3 mol^{-1}, which is in fair agreement with the mean $\Delta V^{\neq}_{\mathrm{A}}$ determined for the other hydrolysis reactions.

Increasing the degree of steric hindrance by introducing a methyl group onto Et$_4$dien in the fourth position decreases the rate of solvolysis/isomerization by a factor of 0.33, but does not affect $\Delta V^{\neq}_{\mathrm{exp}}$, e.g. for Pd(MeEt$_4$dien)SCN$^+$ $\Delta V^{\neq}_{\mathrm{exp}}$ = −9.5 ± 0.5 cm^3 mol^{-1} [209]. Similarly, bromide substitution into this substrate resulted in a $\Delta V^{\neq}_{\mathrm{exp}}$ of −10.5 ± 0.6 cm^3 mol^{-1} [209].

On the basis of rather small differences in $\Delta S^{\neq}_1$ it was suggested [210] that in the "bulky" dipolar aprotic solvents, such as DMSO and DMF, the mechanism of substitution in Pd(Et$_4$dien)X^{n+} complexes becomes more dissociative. It was also observed [210] that the order of reactivity found in protic solvents (i.e. Cl$^-$ > Br$^-$ > I$^-$) was reversed in DMSO and DMF. The assignment of a dissociative mechanism in this paper was further rationalized from a considera-

TABLE 27

Activation parameters for the substitution reactions of $Pd(Et_4dien)I^+$ with Br^- at $\mu = [Br^-] = 0.05$ M and 40°C [211]

Solvent	$\Delta H_1^{\neq}$ (kJ mol^{-1})	$\Delta S_1^{\neq}$ (J K^{-1} mol^{-1})	$(\Delta V_{exp}^{\neq})_1$ (cm^3 mol^{-1})
C_2H_5OH	85 ± 2	−67 ± 8	−12.9 ± 0.4
CH_3OH	83 ± 2	−63 ± 8	−13.4 ± 0.5
H_2O	71 ± 1	−69 ± 3	−11.5 ± 0.2
$(CH_3)_2SO$	82 ± 2	−42 ± 8	−10.1 ± 0.2
$(CH_3)_2NCHO$	82 ± 2	−46 ± 8	−9.3 ± 0.3
CH_3CN	76 ± 4	−78 ± 12	−7.9 ± 0.5

tion of the preference shown by Pd(II) for binding to the softer sulfur of DMSO rather than the oxygen. This would oblige the DMSO molecule to approach the metal center with its plane parallel to that of the complex, thereby increasing the probability of steric interference. The original study [210] was extended to other solvents and included high pressure kinetics [211]. The results of this investigation are summarized in Table 27. These data clearly show that no significant differences exist between the $(\Delta V_{exp}^{\neq})_1$ values in the three dipolar aprotic solvents and the other solvents. Furthermore, the $\Delta S_1^{\neq}$ value for acetonitrile suggests that the somewhat higher values for DMSO and DMF are merely superficial. Thus, a common associative solvolysis mechanism was proposed [211] and the differences in the $(\Delta V_{exp}^{\neq})_1$ were attributed to the varying cross-sectional areas of the solvents at the coordinating oxygen atom. The carbonyl oxygens of DMSO and DMF penetrate the first coordination sphere with less change in the volume of the system than the V-shaped alcohol molecules.

The mechanism of spontaneous isomerization of *cis*-$Pt(PEt_3)_2RX$ to the *trans* isomer in protic solvents is currently a controversial issue (where R =

TABLE 28

Rate data for the isomerization and substitution reactions of *cis*-$Pt(PEt_3)_2RBr$ in methanol at 30°C [214]

R	Isomerization			Substitution		
	$10^3 k_i$ (s^{-1})	$\Delta H_i^{\neq}$ (kJ mol^{-1})	$\Delta S_i^{\neq}$ (J K^{-1} mol^{-1})	$10^3 k_1$ (s^{-1})	$\Delta H_1^{\neq}$ (kJ mol^{-1})	$\Delta S_1^{\neq}$ (J K^{-1} mol^{-1})
C_6H_5	1.07	87.8	−12.5	6000	51.4	−59.3
p-$CH_3C_6H_5$	2.34	81.5	−25.9	4280	47.6	−75.2
o-$CH_3C_6H_5$	0.72	98.6	+20.9	54.4	51.8	−97.8
o-$C_2H_5C_6H_5$	0.55	100.3	+23.8	16.2	54.3	−98.6
2,4,6-$(CH_3)_3C_6H_5$	0.19	67.3	−94.5	0.19	66.9	−94.5

alkyl or substituted aryl groups, and X = Cl or Br). Romeo and co-workers [212—216] have published a series of papers supporting the claim for a dissociative, asynchronous mechanism in which isomerization of the three-coordinate intermediate occurs. Substitution into the substrate was considered to proceed by an associative solvolysis for small, nonsterically restricting R groups, whereas for the more bulky R groups, the reaction is forced into a dissociative mode of activation. In the case of the extremely bulky mesityl ligand (2,4,6-trimethylphenyl), the rates and activation parameters, $\Delta H_i^{\neq}$ and $\Delta S_i^{\neq}$, for substitution and isomerization proved to be identical. For example, the rates and activation parameters for the series where X = Br in methanol are presented in Table 28 [214]. In this case, therefore, the isomerization reactions, as well as the substitution reaction of *cis*-$Pt(PEt_3)_2$(mesityl)Br, obey the following equations [212—216]

$$\textit{cis}\text{-Pt(PEt}_3)_2\text{RBr} \xrightarrow{k_i} \textit{cis}\text{-Pt(PEt}_3)_2\text{R}^+ + \text{Br}^- \tag{62}$$

$$\textit{cis}\text{-Pt(PEt}_3)_2\text{R}^+ \xrightarrow{k_a} \textit{trans}\text{-Pt(PEt}_3)_2\text{R}^+ \tag{63}$$

$$\textit{trans}\text{-Pt(PEt}_3)_2\text{R}^+ + \text{Br}^- \xrightarrow{\text{fast}} \textit{trans}\text{-Pt(PEt}_3)_2\text{RBr} \tag{64}$$

with k_i the observed rate constant in the absence of added Br^-. The presence of bromide ion retards the rate of isomerization and is therefore consistent with the dissociative reaction scheme in which eqn. (62) is rate determining. The nucleophile-independent path of the substitution reaction for R ≠ mesityl is generally accepted as being a solvolysis step in an associative process [212—217]

$$\textit{cis}\text{-Pt(PEt}_3)_2\text{RBr} + \text{MeOH} \xrightarrow{k_1} \textit{cis}\text{-Pt(PEt}_3)_2\text{R(MeOH)}^+ + \text{Br}^- \tag{65}$$

$$\textit{cis}\text{-Pt(PEt}_3)_2\text{R(MeOH)}^+ + \text{Y}^- \xrightarrow{\text{fast}} \textit{cis}\text{-Pt(PEt}_3)_2\text{RY} + \text{MeOH} \tag{66}$$

It was later established that the volumes of activation for isomerization and substitution of *cis*-$Pt(PEt_3)_2$(mesityl)Br in methanol at 30°C are —12.0 ± 0.5 $cm^3\ mol^{-1}$ ($\mu = 0$) [218] and —14.1 ± 0.5 $cm^3\ mol^{-1}$ ($\mu = 0.025$ M) [217]. This virtual equality of the volumes of activation also implies a common mechanism for the two reactions, but the significant negative values could not be rationalized in terms of a dissociative process. They do in fact favor an associative solvolysis in accordance with eqns. (65) and (66). A dissociative mechanism would be expected to yield a $\Delta V_{\text{exp}}^{\neq}$ value of approximately zero due to the counteracting effects of bond separation and a 1 : 1 charge formation.

A re-evaluation [217] of the existing isomerization data [214], including the $[Br^-]$ dependence of the rate of isomerization, showed that, with the exception of R = mesityl, they could be better rationalized in terms of a rapid solvolytic pre-equilibrium, described by K_s, followed by a rate-determining isomerization, k_i, of the *cis*-$Pt(PEt_3)_2R(MeOH)^+$ species, according to the rate equation

$$k_{\mathrm{obs}} = k_i K_s/([\mathrm{Br}^-] + K_s) \tag{67}$$

where, in the absence of added Br^-, $k_{\mathrm{obs}} = k_i$. For R = mesityl, it was suggested [217] that steric hindrance of the incoming methanol molecule must be sufficiently acute as to slow the rate of solvolysis to such an extent that it becomes slower than the isomerization step. The following rate equation could then be formulated,

$$k_{\mathrm{obs}} = k_i k_s/(k_{-s}[\mathrm{Br}^-] + k_i) \tag{68}$$

where k_s and k_{-s} are the forward and reverse rate constants, respectively, for the solvolysis step (eqn. (65)). Again, eqn. (68) reduces to $k_{\mathrm{obs}} = k_s$ when $[\mathrm{Br}^-] = 0$. Thus, according to this concept, the rates of all the substitution reactions and the rate of isomerization of *cis*-$\mathrm{Pt(PEt_3)_2}$(mesityl)Br are solvolysis controlled. The remaining isomerization reactions involve a pre-equilibrium, as described by eqn. (67)

The rate equation proposed for a dissociative mechanism [214] takes the same form as eqn. (68). Nevertheless, the $\Delta S_1^{\neq}$ and $(\Delta V_{\mathrm{exp}}^{\neq})_i$ values give preferential support to an associative solvolytic initial step. Further convincing evidence was provided by extending the pressure dependence of k_{obs} for the isomerization of *cis*-$\mathrm{Pt(PEt_3)_2}$(mesityl)Br to higher pressures than were originally exerted [217], i.e. up to 2 kbar [218]. Whereupon, as illustrated in Fig. 8, ($\ln k_{\mathrm{obs}}$) showed a clear maximum which could only be explained in terms of a consecutive reaction with the two steps being characterized by volumes of activation of opposite sign. In other words, an initial solvolysis step, $(\Delta V_{\mathrm{exp}}^{\neq})_1 = -12$ to -14 cm^3 mol^{-1}, is followed by an isomerization step with a positive $\Delta V_{\mathrm{exp}}^{\neq}$. The latter could result from either a dissociative loss of a

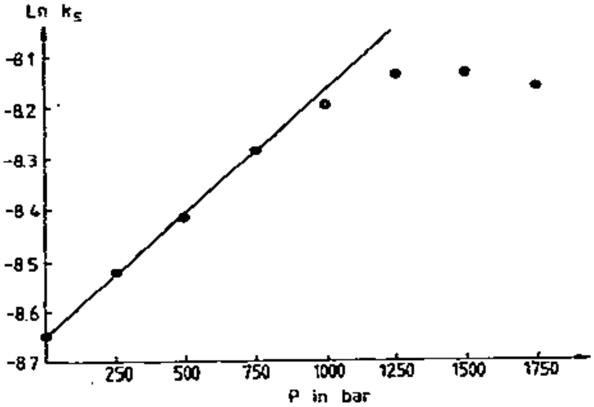


Fig. 8. The pressure dependence of the solvolysis rate constant for the isomerization of *cis*-$\mathrm{Pt(PEt_3)_2}$(mesityl)Br in methanol at 30°C [218].

methanol ligand or an internal rearrangement, conceivably via a tetrahedral intermediate.

By way of a final check of this hypothesis, the activation volume for the isomerization of *cis*-$Pt(PEt_3)_2(C_6H_5)Br$ was measured in methanol in the absence of added Br^- [218]. Not only were the rate constants dependent on the complex concentration, as could be anticipated from the $[Br^-]$ dependence in eqn. (67) cf. the rate constants for the isomerization of the corresponding mesityl complex are independent of complex concentration [217, 218]), $\Delta V^{\neq}_{exp}$ was found to be positive, 7.9 ± 0.6 $cm^3\ mol^{-1}$ [218]. Therefore, although the "normal pressure" kinetic results provided adequate circumstantial evidence for an initial solvolysis step in the isomerization reaction, the complete pressure data are direct and convincing proof for this mechanism.

(ii) Oxidative addition reactions

The pressure dependencies of the rates of oxidative addition of hydrogen [219] and methyl iodide [220] onto Vaska's complex, *trans*-$Ir(PPh_3)_2(CO)Cl$, were studied in a variety of solvents. The oxidative addition reaction takes the general form

$$Ir(PPh_3)_2(CO)Cl + XY \rightarrow Ir(PPh_3)_2(XY)(CO)Cl \qquad (69)$$

where XY = H—H or CH_3—I. The volumes of activation are listed in Table 29 together with the q_p values for the respective solvents [219,220]. In both cases plots of $\Delta V^{\neq}_{exp}$ versus q_p were made, similar to that shown in Fig. 7. With the exception of the solvent $CHCl_3$, which was thought to add to the Vaska complex and thereby complicate the kinetics, good linear relationships were established. The respective values of $\Delta V^{\neq}_{intr}$ obtained from the ordinate intercepts for H_2 and CH_3I addition are —18 and —17 $cm^3\ mol^{-1}$ [219,220]. For XY = H_2, $\Delta V^{\neq}_{intr}$ was considered to be consistent with the simultaneous formation of two Ir—H bonds. This postulate is supported by

TABLE 29

The solvent dependence of the volumes of activation for the oxidative addition reaction between CH_3I/H_2 and $Ir(PPh_3)_2(CO)Cl$ [219,220]

Solvent	$10^6 q_p$ (bar^{-1})	$\Delta V^{\neq}_{exp}$ (CH_3I)[a] ($cm^3\ mol^{-1}$)	$\Delta V^{\neq}_{exp}$ (H_2)[b] ($cm^3\ mol^{-1}$)
Benzene	15.6	—29.8	
Chloroform	15.0	—19.2	
Toluene	14.7	—28.2	—20.4
Chlorobenzene	8.9	—23.6	—19.0
Acetone	5.4	—20.5	
Dimethylformamide	1.7	—15.2	—18.0

[a] At 25°C. [b] At 10°C.

the fact that the H ligands are in a *cis* configuration in the final product. On the other hand, for XY = CH_3I a "linear" transition state was proposed [220] with the formation of an Ir—carbon bond.

D. REACTIONS OF TETRAHEDRAL COMPLEXES

(i) Ligand exchange reactions

To our knowledge the only reaction studied under high pressure to date involves the exchange of triphenylphosphine (TPP) with $Co(TPP)_2Br_2$ in deutero-chloroform [221]. This ^{1}H NMR investigation yielded the parameters, $\Delta V^{\neq}_{exp} = -12.1 \pm 0.6$ cm^3 mol^{-1} and $\Delta\beta^{\neq} = -3.3 \pm 0.5$ cm^3 mol^{-1} kbar^{-1} at 30°C. These results complement an earlier temperature dependence study [222] which gave the values $\Delta H^{\neq} = 32 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = -80 \pm 13$ J K^{-1} mol^{-1}. The observed second-order kinetics and the negative $\Delta V^{\neq}_{exp}$ and $\Delta S^{\neq}$ values are in keeping with an associative process. Partial bonding of the free phosphine was expected to result in $\Delta V^{\neq}_{exp}$ values between −5 and −16 cm^3 mol^{-1} [221] and therefore an I_a mechanism was assigned.

E. CONCLUSIONS

This review was meant to give an insight into the subject of high pressure inorganic kinetics and hopefully covers the relevant literature up until the middle of 1979. However, certain new or fringe topics have not been treated. The former includes high pressure photochemistry of coordination compounds which is only in its infancy [223]. Another important topic which has not been discussed deals with the application of high pressure techniques to biochemical systems [26,224,225].

It is, however, hoped that the compilation of high pressure kinetic data convincingly proves the utility of volumes of activation as criteria in the discussion of reaction mechanisms of coordination compounds.

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