# INTERPRETATION OF THE VOLUME OF ACTIVATION OF

# INORGANIC REACTIONS IN SOLUTION

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## 1. Introduction

The interpretation of activation and reaction volumes of organic systems in solution has received wide attention and was reviewed extensively in the past.[1-3] In contrast. only a few summarizing papers on the elucidation of inorganic reaction mechanisms by high pressure kinetic studies have appeared.[4-8] A complete review on the activation volumes of the reactions of transition metal compounds in solution, is in press.[9] All these reports have clearly shown the usefulness of volume of activation data as a criterion for the discussion of mechanisms of reactions in solution.

In this paper we intend to give a critical appraisal of the interpretation of volumes of activation of inorganic reactions in solution. by illustrating the main arguments used in such interpretations and by emphasizing the problem areas. Therefore. this paper is by no means a complete review of the present status of high pressure inorganic mechanistic studies. We shall rather concentrate in our discussion on typical illustrative examples wherever these are available.

## 2. Volume Quantities of Chemical Reactions in Solution – Definitions and Determinations

If we consider a chemical reaction of the type

$$A + B \xrightarrow{k} AB.$$

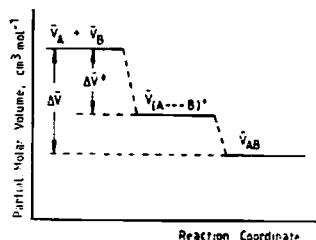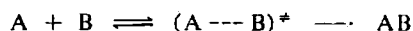186                                          R.V. Eldik and H. Kelm
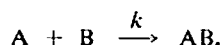


Fig. 1. Volume profile diagram for the reaction
$A + B \rightleftharpoons (A --- B)^* \longrightarrow AB$.

the simplest conceivable mechanism can be formulated according to the transition state theory[10] as follows:

$$A + B \rightleftharpoons (A --- B)^{\neq} \longrightarrow AB$$

Such a reaction can in general be presented by a volume profile diagram as shown in Fig. 1. The magnitude and sign of the overall partial molar volume change, $\Delta \bar{V} = \bar{V}_{AB} - \bar{V}_A - \bar{V}_B$, and of the volume of activation, $\Delta \bar{V}^{\neq} = \bar{V}_{(A \cdots B)}^{\neq} - \bar{V}_A - \bar{V}_B$, depend on the nature of the chemical species involved and their environmental stabilization.

The reaction volume ($\Delta \bar{V}$) can be determined directly by dilatometry or can be estimated from a combination of the partial molar volumes of the reactant and product species according to the above expression. In turn, the partial molar volume of a stable species can be obtained by extrapolating the apparent molar volume to infinite dilution. The latter is usually determined from density measurements of dilute solutions using a digital densimeter. Certainly, $\Delta \bar{V}$ can also be derived from the pressure dependence of the equilibrium constant $K$ according to $(d\ln K/dP)_T = -\Delta \bar{V}/RT$.

The volume of activation ($\Delta \bar{V}^{\neq}$) can only be determined from the effect of pressure on the rate constant ($k$) of the reaction under investigation, i.e.,

$$\Delta \bar{V}^{\neq} = -RT(d\ln k/dP)_T.$$

In principle $\Delta \bar{V}^{\neq}$ depends on pressure, i.e., the slope of $\ln k$ versus $P$ decreases with increase in pressure, and the compressibility coefficient of activation, $\Delta \beta^{\neq}$, has therefore been defined as

$$\Delta \beta^{\neq} = -(d\Delta \bar{V}^{\neq}/dP)_T.$$

In order to have a basis for comparison with other activation parameters, $\Delta \bar{V}^{\neq}$ values are normally reported at zero pressure. Since the actual relationship between $k$ and $P$ is unknown, various mathematical descriptions have been proposed,[8,9,11] of which the following one has been used extensively to describe the pressure dependence of $\ln k$ for inorganic systems,

$$\ln k = a + bP + cP^2 = \ln k_0 + bP + cP^2.$$

For $P=0$ it follows that $\Delta \bar{V}_0^{\neq} = -bRT$ and $\Delta \beta^{\neq} = 2cRT$. It must, however, be emphasized that for systems in which $\Delta \bar{V}^{\neq}$ strongly depends on pressure, the selection of an appropriate $k=f(P)$ function leads to some fluctuations in the obtained values of $\Delta \bar{V}_0^{\neq}$.[9,11]

Various instruments suitable for the measurement of $k$ as a function of $P$ have been

developed and reviewed in detail elsewhere.[1,9] In general, a pressurized batch reactor with a special sampling valve is used for the study of slow reactions under pressure. from which samples are taken at regular time intervals and analysed according to suitable analytical procedures.[12] For faster reactions, "*in-situ*" systems have been developed employing spectrophotometric, conductometric and NMR techniques,[13-15] which include the recent addition of high-pressure stopped flow and T-jump techniques.[16-19]

Whatever the experimental procedure adopted for the determination of $\Delta \bar{V}^{\neq}$, it must be very accurate and highly reproducible. Precise temperature control is a further important requirement since the change in $k$ with change in $P$ is rather small *viz.*. approx. 20% per 500 bar for $\Delta \bar{V}^{\neq} = 10 \text{ cm}^3 \text{ mol}^{-1}$ compared to a change in $k$ of approx. 15% per °C for $\Delta H^{\neq} = 20$ kcal mol$^{-1}$.

## 3.   Interpretation of Volume of Activation

It is generally accepted by high pressure kineticists that the experimentally observed $\Delta \bar{V}^{\neq}$ consists of two components: an intrinsic part ($\Delta V_{intr}^{\neq}$). which describes the change in volume due to changes in bond lengths and angles. and a solvational part ($\Delta V_{solv}^{\neq}$). which describes the change in volume due to changes in solvation during the activation process. For systems in which the solute-solvent interactions are predominantly of electrostatic nature. the solvation contribution is also referred to as electrostriction.

Experimentally, both contributions are measured simultaneously and $\Delta \bar{V}^{\neq}$ is a composite value. The sign of the two components can be predicted as illustrated by the simplified schemes in Fig. 2. $\Delta V_{intr}^{\neq}$ is thus the indicative part relevant for the discussion of the intimate mechanism. In reactions of high polarity changes, $\Delta V_{solv}^{\neq}$ may be much larger than $\Delta V_{intr}^{\neq}$ and can in fact counteract and more than compensate the $\Delta V_{intr}^{\neq}$ term. Thus additional measurements and/or theoretical estimations are then necessary to deduce the magnitude of $\Delta V_{solv}^{\neq}$. in order to obtain the meaningful $\Delta V_{intr}^{\neq}$ value.

One method of elucidating $\Delta V_{intr}^{\neq}$ is to study the solvent dependence of $\Delta \bar{V}^{\neq}$ for reactions in which charge creation or charge quenching occurs during the activation process. In such
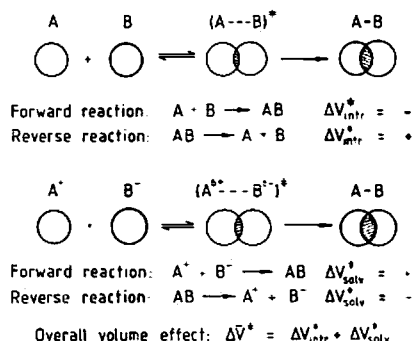


Fig. 2. Simplified examples to illustrate the sign of the components of $\Delta \bar{V}^{\neq}$.

cases $\Delta V_{solv}^{\neq}$ will contribute significantly to $\Delta \bar{V}^{\neq}$ and it is expected to be very sensitive towards the nature of the solvent. A suitable extrapolation of the $\Delta \bar{V}^{\neq}$ data as a function of solvent allows the estimation of $\Delta V_{intr}^{\neq}$. Furthermore, theoretical descriptions of the solvent effects on the rates of reactions can be employed to predict $\Delta V_{solv}^{\neq}$ with some accuracy.[20] If it is justified to assume that the electrostatic interaction of ionic charges and of dipoles contribute most to the main component of $\Delta V_{solv}^{\neq}$, equations proposed by Born and Kirkwood[21] can be used to describe the ionic and dipolar effects of such an interaction. It was illustrated that for reactions with strong dipolar changes the solvent dependence of $\Delta \bar{V}^{\neq}$ can be described by the solvent characterizing parameter $q_p = d[(D-1)/(2D+1)]/dP$, where $D$ = dielectric constant of the medium. For the substitution reaction of $trans$-[Pt(py)$_2$(Cl)(NO$_2$)] with pyridine in CH$_3$NO$_2$, CH$_3$OH, C$_2$H$_5$OH and CH$_2$Cl$_2$, a plot of $\Delta \bar{V}^{\neq}$ versus $q_p$ presented a straight line[14] with the intercept $\Delta V_{intr}^{\neq}$. However, for many inorgaic systems the solvent variation is often limited or even restricted by the solubility limits of the reactants in the respective solvents.

The evaluation of the compressibility coefficient, $\Delta \beta^{\neq}$, as an indication of the $\Delta V_{solv}^{\neq}$ contribution was suggested by Stranks.[1] It is accepted[11] that $\Delta V_{intr}^{\neq}$ is virtually pressure independent over the limited pressure range (up to 3 kbar) usually used for the determination of $\Delta \bar{V}^{\neq}$. However, $\Delta V_{solv}^{\neq}$ is expected to be pressure dependent and should therefore reflect as $\Delta \beta^{\neq}$, which can sometimes be correlated with the compressibility of the solvent.

At this point it should be emphasized that the experimental determination of $\Delta \beta^{\neq}$, i.e., the pressure dependence of $\Delta \bar{V}^{\neq}$, is subjected to significant errors. In principle, such a determination is analogous to the measurement of the temperature dependence of $\Delta H^{\neq}$ (also second derivative) i.e., $\Delta C_p^{\neq}$, which can only be obtained from extraordinarily accurate rate data. However, one must keep in mind that the fundamental physical concept of the pressure dependence of the rate constant suggests that $\Delta \bar{V}^{\neq}$ should be pressure dependent and therefore larger effects are expected. Nevertheless, depending on the analytical method employed and the order of rate of the reaction concerned, the observed rate constants as a function of pressure may include relatively large errors. To distinguish between experimental error or curvature in the ln$k$ versus $P$ plots then becomes a matter of personal choice.[22] This situation is very similar to the question of curvature or none curvature in the $k_{obs}$ versus [entering ligand] plots for anation reactions of octahedral complex ions, which is considered as kinetic evidence for the participation of ion-pairs in the mechanism. Our own experience has shown that in some cases the rate data at $P \geq 500$ bar exhibit a perfect linear ln$k$ versus $P$ plot over the range investigated, but that the data points at lower pressures slightly deviate from this line. This could be attributed to a non-chemical phenomenon of no mechanistic meaning. With the experimental uncertainties in the $k = f(P)$ data it is probably advisable to only estimate the *minimum* values of $\Delta \beta^{\neq}$ and thus for $\Delta V_0^{\neq}$, as obtained from the application of a linear correlation.

Asano[23] recently suggested a new method to estimate $\Delta V_{intr}^{\neq}$ directly from the pressure depenence of $k$ in which the Tait equation is used to describe the isothermal compression of

the solvent. According to the derived equation

$$-\frac{RT}{P-1}\ln\frac{k_P}{k_1} = JV_{intr}^{\neq} - \frac{\kappa}{P-1}\ln\frac{B+P}{B+1,}$$

in which $B$ is a characteristic solvent parameter, the left hand side is plotted against $\frac{1}{P-1}\ln$ $\frac{B+P}{B+1}$ and $JV_{intr}^{\neq}$ is then obtained directly from the intercept of the line. The advantage of this method is that $JV_{intr}^{\neq}$ can be estimated in a fairly easy manner and one does not need to measure an extensive solvent-pressure dependence of the reaction. Asano tested his method with a number of inorganic and organic systems and obtained $JV_{intr}^{\neq}$ values which appear to be realistic. Since $(dV/dP)_T$ is used by Asano as solvent characterizing parameter, his approach is expected to be primarily successful for non-polar reactions. In reactions with predominatly electrostatic interactions, $(dD/dP)_T$ should be adopted as solvent describing parameter unless $(dV/dP)_T$ is proportional to $(dD/dP)_T$, which was shown to be valid for some solvents over a limited pressure range.

Another important variable to keep in mind in the interpretation of $JV^{\neq}$ values, is temperature. In general, $JV^{\neq}$ increases with increase in temperature based on the results obtained for a limited number of systems studied quantitatively in this respect. The results confirmed the Maxwell relation

$$-\left[\frac{d(JV^{\neq})}{dT}\right]_P = \left[\frac{d(JS^{\neq})}{dP}\right]_{T,}$$

which is interpreted[24-27] as evidence for the existence of an equilibrium system and that no change in mechanism occurs over the investigated pressure and temperature ranges. Since $JV^{\neq}$ data are often obtained at quite different temperatures—the temperature mostly chosen with the intention to reach a reasonable time scale for the experiments—the comparison of their absolute values should be made with the necessary caution.

Likewise the influence of ionic strength on the value of $JV^{\neq}$ should be considered. especially when the latter is compared with reaction and partial molar volumes determined under completely different ionic strength conditions. At least it appears to be necessary to obtain some information about the sensitivity of $JV^{\neq}$ on ionic strength. In some cases. *viz.*, the anation of $Cr(NH_3)_5OH_2^{3+}$ by $NCS^-$,[22] and the hydrolysis of $Pt(dien)X^+(X=Cl, Br)$,[28] it was found that the influence of ionic strength is rather small and of the order of the experimental error involved in the measurement of $JV^{\neq}$. *i.e.*, *ca.* 1 cm$^3$ mol$^{-1}$ for an increase in ionic strength of 1 M.

So far the determination and interpretation of $JV^{\neq}$ was based on the assumption of an elementary, one-step reaction going essentially to completion. However, in many cases more complicated reaction schemes are encountered with the consequence that additional care must be taken to separate the complex quantities. If for instance the system includes two first order opposing reactions

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$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$
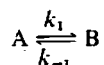
the observed rate constant $k_{obs} = k_1 + k_{-1}$, such that the measured $\Delta V^{\neq}$ will be a composite of the volumes of activation for both reactions. A separation can only be achieved by either measuring the pressure dependence of both reactions separately, $i. e.$ by adopting an initial rate procedure, or by measuring the pressure dependence of the overall equilibrium constant $K (= k_1/k_{-1})$, from which $\Delta V = \Delta V^{\neq}(k_1) - \Delta V^{\neq}(k_{-1})$ can be obtained.

In many systems the rate-determining step is preceded by a rapid protonation/deprotonation or ion-pair formation equilibrium

$$A + B \overset{K}{\rightleftharpoons} AB \overset{k}{\longrightarrow} C$$
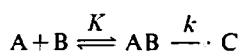
such that $k_{obs} = kK$. For such a system the measured $\Delta V^{\neq}$ equals $\Delta V(K) + \Delta V^{\neq}(k)$, and the required $\Delta V^{\neq}(k)$ can only be obtained if $\Delta V(K)$ is known. It follows that the interpretation of $\Delta V^{\neq}$ for more complex mechanisms becomes rather difficult, and efforts should be made to simplify the investigated system and corresponding rate equations by studying individual steps separately.

More information concerning the interpretation of $\Delta V^{\neq}$ for inorganic reaction system has been obtained from plots of $\Delta V^{\neq}$ $versus$ $\Delta V$, and from volume equation calculations,[7,9,29-31] as will be illustrated in the next section together with the appropriate examples. Due to the composition of $\Delta V^{\neq}$ and $\Delta V$, a (linear) correlation of these quantities may reflect a certain similarity between the transition state and the initial or final states of the reaction in the sense of an "early" or "late" transition state. The requirement of accurate data for such a comparison does not need to be expressed here again. Very similar, in volume equation calculations where $\Delta V^{\neq}$ is related to the partial molar volumes of initial and transition state species, one often deals with a small difference between large values. Small errors in the $\bar{V}_i$ values introduce considerable errors in such calculations, and the obtained results should be interpreted with critical care.

In the following section the interpretation of $\Delta V^{\neq}$ for various types of inorganic reaction systems will be described and discussed in detail in connection with some illustrative and representative examples.

## 4. Volume of Activation of Inorganic Reactions

### 4-1. *Substitution reactions*

Most of the substitution reactions discussed in this section proceed in their rate-determining step $via$ a bond-making or bond-breaking process. Thus a general classification of these intimate mechanistic steps was developed, which may be useful to be characterized first before subdividing the reaction types. In the following table the type of elementary step, the notation of the process, and the character of the transition state are correlated:

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| Type | Notation | Transition state character |
|------|----------|---------------------------|
| Dissociative | D | leaving group completely separated |
| Interchange | $I_d$ | bond breaking is predominant |
|  | $I_a$ | bond making is predominant |
| Associative | A | entering group completely bonded |

Furthermore, a schematic representation of the mechanisms is presented in Fig. 3. In addition to the dissociative (D) and associative (A) modes of activation frequently referred to in organic reactions, inorganic kineticists have introduced[32] the concept of interchange mechanisms (I) in which an encounter complex (viz., ion-pair) is rapidly formed before ther ate-determining activation step takes place, which can either be associative ($I_a$) or dissociative ($I_d$) in character. According to arguments presented in detail before,[7,9] the signs and
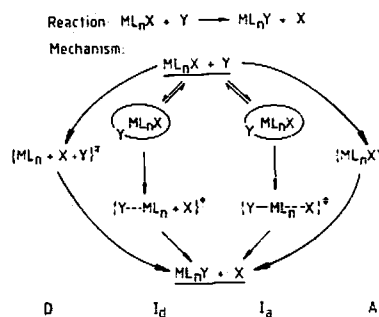


Fig. 3. Schematic representation of the possible inorganic substitution mechanisms

Table 1. Classification of mechanisms for the reaction $ML_nX + Y \longrightarrow ML_nY + X$

| Properties | Mechanism | | | |
|------------|-----------|-----------|-----------|-----------|
|  | D | $I_d$ | I | A |
| M-X bond | broken | substantially stretched | partially stretched | intact |
| M-Y bond | not formed | partially formed | substantially formed | formed |
| $\Delta S^*$ | large positive | small | small | large negative |
| $\Delta V_{intr}^*$ | positive | small positive | small negative | negative |
| $\Delta \bar{\beta}^{*}$ | positive | small | small | negative |

* for solvent exchange reactions, $X = Y = $ solvent.

magnitudes of $\Delta V_{intr}^*$ and $\Delta \bar{\beta}^*$ for the different mechanisms are expected to be as summarized in Table 1. The often rather delicate differentiation between $I_a$ and $I_d$ has led to some dispute in the literature.[22]

The most simple type of substitution reactions are ligand exchange reactions of the form

$$ML_n + L^* \longrightarrow ML_{n-1}L^* + L,$$
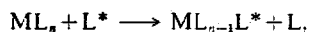
in which L and L* are both solvent molecules. No net change in charge occurs during this exchange process, such that negligible solvational changes are expected and $\Delta V_{solv}^* \simeq 0$, i.e., $\Delta \bar{V}^* \simeq$

$\Delta V_{intr}^{\neq}$. The earliest solvent exchange systems studied under pressure[33-35] were water exchange reactions of the $M(NH_3)_5OH_2^{3+}$ species, where $M = Co(III)$, $Rh(III)$, $Cr(III)$ and $Ir(III)$. The experimental values reported for $\Delta V^{\neq}$ are $+1.2\pm0.2$, $-4.1\pm0.4$, $-5.8\pm0.1$ and $-3.2\pm0.1$ cm³ mol⁻¹, respectively, of which the first is considered as evidence for an $I_d$ mechanism and the others as evidence for $I_a$ mechanisms. In addition it was found that $\Delta V^{\neq}$ had no detectable pressure dependence over the pressure range investigated (i.e., $\Delta\beta^{\neq}\simeq0$), which is in line with the arguments presented earlier. Very similar results were reported[36] for the water exchange reaction of trans-$Co(en)_2(OH_2)_2^{3+}$, viz., $\Delta V^{\neq} = +5.9\pm0.2$ cm³ mol⁻¹ and $\Delta\beta^{\neq}\simeq0$, and were interpreted as indication for an $I_d$ mechanism. Such studies were recently extended to the water exchange reactions of $M(OH_2)_6^{2+}$ species.[37,38] with results of $\Delta V^{\neq} = +7.1\pm0.2$ and $-6.2\pm0.2$ cm³ mol⁻¹ (with $\Delta\beta^{\neq}\simeq0$ in both cases) for $M = Ni(II)$ and $Mn(II)$, respectively, again indicating an $I_d$ or $I_a$ mechanism.

Pressure-independent activation volumes were also reported for solvent exchange reactions in non-aqueous solvents. $\Delta V^{\neq} = -11.3\pm1.0(75°C)$ and $-6.3\pm0.2(65°C)$ cm³ mol⁻¹ for the exchange of DMSO in $Cr(DMSO)_6^{3+}$,[39] and of DMF in $Cr(DMF)_6^{3+}$,[40] respectively, both consistent with an $I_a$ mechanism. The exchange of DMSO in $Co(NH_3)_5DMSO^{3+}$ proceeds[41] with a $\Delta V^{\neq}$ value of $+10.0\pm1.2$ cm³ mol⁻¹ at 45°C and confirms the assignment of an $I_d$ mechanism. Similarly, DMF exchange in $Co(NH_3)_5DMF^{3+}$ and $Rh(NH_3)_5DMF^{3+}$ yielded $\Delta V^{\neq}$ values of $+3.2\pm1.2(55°C)$ and $-1.4\pm0.2(45°C)$ cm³ mol⁻¹, respectively.[42] These results underline the general mechanistic behaviour of the metal ions as experienced with the aquo exchange reactions. Merbach and co-workers[43,44] reported an associative-dissociative changeover in mechanism for methanol exchange on $M(CH_3OH)_6^{2+}$ along the first-row of transition metals. They reported $\Delta V^{\neq}$ values of $-5.0\pm0.2(Mn^{2+})$, $+0.4\pm0.3(Fe^{2+})$, $+8.9\pm0.3(Co^{2+})$ and $+11.4\pm0.6(Ni^{2+})$ cm³ mol⁻¹, which illustrate the changeover from $I_a$ to $I_d$. Very similar $\Delta V^{\neq}$ values were also reported[43,45] for the exchange of DMF and $CH_3CN$ in $Ni(solv)_6^{2+}$ and $Co(solv)_6^{2+}$. Volumes of activation for the exchange of DMSO and DMF on $Al^{3+}$ and $Ga^{3+}$ are strongly positive[46] and are accompanied by slightly positive $\Delta\beta^{\neq}$ values, altogether pointing to the dissoiative character of the exchange mechanism.
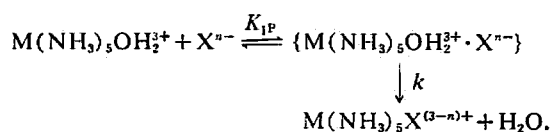
Ligand exchange reactions of the type

$$MX_5L + L^* \rightleftharpoons MX_5L^* + L,$$

in which L and $L^*$ are both uncharged non-solvent molecules, have been studied under pressure for $M = Nb(V)$, $Ta(V)$ and $X = Cl$, Br in $CH_2Cl_2$ and $CHCl_3$.[47] Positive volumes of activation (between $+15.2$ and $+30.5$) were found for $L = Me_2O$, MeCN, $Me_3CCN$, $(MeO)-Cl_2PO$ and $(Me_2N)_3PS$, whereas negative $\Delta V^{\neq}$ values (between $-10.7$ and $-19.8$) were obtained for $L = Me_2S$, $Me_2Se$ and $Me_2Te$. The positive $\Delta V^{\neq}$ values are interpreted as evidence for a D mechanism, whereas the negative values indicate an $I_a$ mechanism. Thus a dissociative-associative crossover is observed in the exchange mechanism, which is in agreement with earlier kinetic observations at normal pressure.[48-50] $\Delta V^{\neq}$ for the exchange of triphenylphosphine

(TPP) with the tetrahedral $Co(Br)_2(TPP)_2$ complex in deuteriochloroform was reported[51] to be $-12.1\pm0.6$ cm$^3$ mol$^{-1}$ and interpreted as evidence for an $I_a$ mechanism. Furthermore, a significant negative $\Delta\beta^*$ value was observed, which underlines the associative character of the exchange process.

One should, however, keep in mind that for the octahedral ligand exchange reactions discussed so far, it was assumed that they proceed without major solvational changes. This assumption was based on the fact that the exchanging ligands are uncharged and it is supported by the evidence that $\Delta\beta^*\simeq0$. In the case of the tetrahedral ligand exchange reaction the substantial $\Delta\beta^*$ value may indicate that major solvational changes occur during the reaction. In addition, the mechanistic interpretation of small absolute values of $\Delta\bar{V}^*$ involves an inherent uncertainty in view of the experimental errors.

More complex inorganic substitution reactions include: anation, ligand substitution, aquation/solvolysis, and base hydrolysis processes. Some typical examples of octahedral and square planar systems have been chosen for the following discussion.

During anation reactions, aquo ligands are replaced by entering nucleophiles, usually according to an interchange mechanism (I) in which the rate-determining interchange step is preceded by an ion-pair formation between the reactant species. A typical example is

$$M(NH_3)_5OH_2^{3+}+X^{n-}\overset{K_{IP}}{\rightleftharpoons}\{M(NH_3)_5OH_2^{3+}\cdot X^{n-}\}$$
$$\downarrow k$$
$$M(NH_3)_5X^{(3-n)+}+H_2O.$$

for which $K_{IP}$ =ion-pair formation constant, $k$ =interchange rate constant and

$$k_{obs}=\frac{k\ K_{IP}\ [X^{n-}]}{1+K_{IP}\ [X^{n-}]}.$$

$K_{IP}$ is in many cases rather small, such that $1+K_{IP}\ [X^{n-}]\sim1$ and $k_{obs}=kK_{IP}\ [X^{n-}]$. The observed $\Delta\bar{V}^*$, calculated from the pressure dependence of the second-order rate constant $kK_{IP}$, is the sum of $\Delta\bar{V}_{IP}$ and $\Delta\bar{V}_i^*$. For the systems: M=Co(III), $X^{n-}$=Cl$^-$; M=Co(III), $X^{n-}$=SO$_4^{2-}$; M=Rh(III), $X^{n-}$=Cl$^-$, and M=Cr(III), $X^{n-}$=NCS$^-$, pressure independent $\Delta\bar{V}^*$ values of $+1.4\pm0.8(60°C)$, $+2.3\pm1.8(60°C)$, $+3.0\pm0.7(60°C)$ and $-4.9\pm0.6(50°C)$ cm$^3$ mol$^{-1}$, respectively, were reported.[22] Since these values were determined at high temperatures and high ionic strengths, it was argued that $\Delta\bar{V}_{IP}$ and $\Delta V_{solv}^*$, respectively, should be minimal and that the measured values are those for $\Delta V_{intr}^*$ of the rate-determining interchange step. This means that all the studied anation reactions are of the $I_d$ type, with the exception of the anation of $Cr(NH_3)_5OH_2^{3+}$ by NCS$^-$. Very similarly, $\Delta\bar{V}^*$ values[52] of $+4.8\pm0.2$ and $+4.6\pm0.4$ cm$^3$ mol$^{-1}$ for the anation of $cis$-Co(en)$_2$(OH$_2$)$_2^{3+}$ by $H_2C_2O_4/HC_2O_4^-$ and of $cis$-Co(en)$_2$(OH)(OH$_2$)$^{2+}$ by $C_2O_4^{2-}$, respectively, were interpreted as evidence for an $I_d$ mechanism, although a later investigation[53] pointed at a specific nitrate ion catalysis of these reactions. In the case of a purely associative (A) anation reaction $\Delta\bar{V}^*$ is strongly negative as illustrated for the anation of $Ru(NH_3)_5OH_2^{3+}$ by Cl$^-$, for which $\Delta\bar{V}^*=-20\pm1.4$ cm$^3$ mol$^{-1}$ at 60°C.[54]

In a number of anation reactions the process follows a purely dissociative (D) mechanism and no contribution from $\Delta V_{solv}^{\pm}$ is expected since the leaving group is uncharged. For instance, $\Delta \bar{V}^{\pm}$ for the anation of $Co(CN)_5OH_2^{2-}$ by $Br^-$, $I^-$ and $NCS^-$ was found[55] to be $+8.4\pm1.0$, $+9.4\pm1.6$ and $+8.2\pm0.9$ cm$^3$ mol$^{-1}$, respectively. Similarly, $\Delta \bar{V}^{\pm} = +15.7\pm6.5$ and $+14.7\pm 1.6$ cm$^3$ mol$^{-1}$ for the anation of cis-$RhCl_4(OH_2)_2^-$ and $RhCl_5(OH_2)^{2-}$ by $Cl^-$, respectively.[56] These values are very typical and reflect Co-OH$_2$ and Rh-OH$_2$ bond breaking in the dissociative step to form a five-coordinate intermediate.
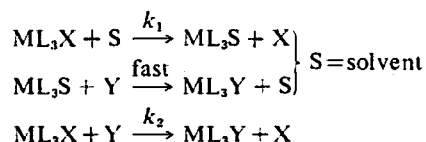
Only a few anation reactions of square planar complexes have been studied under pressure to date. Species such as $Pd(Et_4dien)(OH_2)^{2+}$ and $Pt(dien)(OH_2)^{2+}$ are solvolytic interme- diates in the substitution reactions of $Pd(Et_4dien)X^+$ and $Pt(dien)X^+$, respectively, and react very fast. $\Delta \bar{V}^{\pm}$ for the anation of $Pd(4\text{-Me-}1, 1, 7, 7\text{-Et}_4$ dien$)(OH_2)^{2+}$, $Pd(1, 1, 7, 7\text{-Et}_4$- dien$)(OH_2)^{2+}$ and $Pd(1, 1, 4\text{-Et}_3dien)(OH_2)^{2+}$ by $Cl^-$ was found[17,57] to be $-7.7\pm0.5$, $-3.0 \pm0.2$ and $-2.7\pm0.2$ cm$^3$ mol$^{-1}$, respectively. These $\Delta \bar{V}^{\pm}$ values are taken as evidence for an $I_a$ mechanism.

During ligand substitution reactions of the most general type a ligand X is replaced by a stronger nucleophile Y according to the reaction

$$ML_nX + Y \longrightarrow ML_nY + X.$$
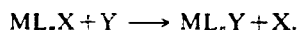
Only a few octahedral systems have been studied under pressure. For instance, an average $\Delta \bar{V}^{\pm}$ value of $+20.6\pm0.4$ cm$^3$ mol$^{-1}$ was reported[58] for the reactions of $Fe(CN)_5(3, 5\text{-Me}_2$ py$)^{3-}$ with cyanide. pyrazine and imidazole, and for the reaction of $Fe(CN)_5(3\text{-CN-py})^{3-}$ with cyanide. This large positive and nucleophile independent value of $\Delta \bar{V}^{\pm}$ underlines that a D mechanism is operating in which $Fe(CN)_5^{2-}$ is produced in the transition state. Similarly, a $\Delta \bar{V}^{\pm}$ value of approx. $+20$ cm$^3$ mol$^{-1}$ for the substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ with hydroxide and cyanide ion[59] also indicates that a primarily dissociative mechanism is prevailing.

Considerably more ligand substitution reactions of square planar complexes have been studied under pressure. In general such reactions proceed according to the mechanism

$$ML_3X + S \xrightarrow{k_1} ML_3S + X$$
$$ML_3S + Y \xrightarrow{fast} ML_3Y + S \quad \left.\right\} S = solvent$$
$$ML_3X + Y \xrightarrow{k_2} ML_3Y + X$$

for which

$$k_{obs} = k_1 + k_2[Y].$$

We will, however, at this stage only concentrate on the pressure dependence of $k_2$, which represents the direct attack of Y, and can therefore be classified as a ligand substitution (Y for X) reaction. The pressure dependence of the solvolysis step ($k_1$) will be discussed in the next section which deals with the aquation/solvolysis reactions of inorganic complex species. The $k_2$ path is generally accepted to be of an associative nature (A or $I_a$) and this has been substantiated by high pressure studies. The substitution rate of chloride by pyridine in the

Table 2.  Volumes of activation for the reaction[a]
$$Pt(dien)X^+ + Y \longrightarrow Pt(dien)Y^+ + X$$

| X | Y | $\Delta \bar{V}^{\ast}$ cm$^3$ mol$^{-1}$ |
|---|---|---|
| Br$^-$ | N$_3^-$ | $- 8.5 \pm 0.2$ |
| Br$^-$ | py | $- 7.7 \pm 0.5$ |
| Br$^-$ | NO$_2^-$ | $- 6.4 \pm 0.7$ |
| Cl$^-$ | N$_3^-$ | $- 8.2 \pm 1.3$ |
| I$^-$ | N$_3^-$ | $- 8.2 \pm 0.7$ |
| N$_3^-$ | I$^-$ | $-12.2 \pm 0.1$ |
| N$_3^-$ | SCN$^-$ | $- 7.3 \pm 0.1$ |

[a] Temp.$=25^{\circ}$C, ionic strength$=0.2$ M, data reported in Ref. (60).

complex *trans*-Pt(py)$_2$(NO$_2$)(Cl) was measured as a function of pressure in CH$_3$NO$_2$, CH$_3$OH. C$_2$H$_5$OH and CH$_2$Cl$_2$.[10] The obtained $\Delta \bar{V}^{\neq}$ values are such that $\Delta \bar{V}^{\neq}$ plotted against $q_p$ (the solvent characterizing parameter) for various solvents gives a linear plot from which it follows that $\Delta V_{intr}^{\neq} = -4 \pm 1$ cm$^3$ mol$^{-1}$. This illustrates the associative character of the process. and the large contribution of $\Delta V_{solv}^{\neq}$ is mainly due to changes in dipole moment during the activation process.  Another series of reactions studied in detail[60] is presented by

$$Pt(dien)X^+ + Y \longrightarrow Pt(dien)Y^+ + X,$$
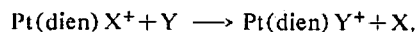
for which the results are summarized in Table 2. It follows that $\Delta \bar{V}^{\neq}$ is independent of the leaving group and mainly depends on the nature of the entering ligand. which is within expectations for an associative (A) mechanism.  Furthermore. $\Delta V_{solv}^{\neq}$ is apparently small since $\Delta \bar{V}^{\neq}$ is approximately the same for neutral and charged nucleophiles.  In a study of the corresponding substitution reactions of the sterically hindered Pd(1, 1, 7, 7-Et$_4$dien)X$^+$ species. $\Delta \bar{V}^{\neq}$ values of $-15.5 \pm 0.8$(X=Cl$^-$, Y=N$_3^-$), $-2.6 \pm 0.5$(X=Cl$^-$, Y=SCN$^-$) and $-10.1 \pm 0.1$(X=Br$^-$, Y=SCN$^-$) cm$^3$ mol$^{-1}$ were reported.[61]  These data illustrate that $\Delta \bar{V}^{\neq}$ is a function of both the leaving and entering groups, in contrast to the Pt(dien)X$^+$ system.  This was interpreted as evidence for an interchange (I) mechanism. but the differentiation between I$_a$ or I$_d$ is uncertain at this stage. especially since $\Delta \bar{V}^{\neq}$ is a composite of $\Delta V_{intr}^{\neq}$ and $\Delta V_{solv}^{\neq}$. Finally it should be mentioned that for ligand substitution reactions of highly sterically crowded Pt(II) complexes of the type Pt(PEt$_3$)$_2$(R)(Br). where R$=2$. 4. 6-Me$_3$C$_6$H$_2$. $\Delta \bar{V}^{\neq}$ values between $-12$ and$-16$ cm$^3$ mol$^{-1}$ were reported[62] for the replacement of Br$^-$ by I$^-$ and SC(NH$_2$)$_2$ in methanol.  Similar results were also found[63] for the reactions with SC(NH$_2$)$_2$ in EtOH and DMSO.  All of these were interpreted as a strong indication for an associative (A or I$_a$) mechanism. notwithstanding the steric crowding at the metal centre.

We now turn to a discussion of $\Delta \bar{V}^{\neq}$ for the aquation reactions of octahedral complexes. The following system has been studied in great detail[29,31,64,65]

$$M(NH_3)_5 X^{(3-n)+} + H_2O \longrightarrow M(NH_3)_5 OH_2^{3+} + X^{n-},$$
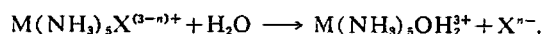
$M = Co(III)$: $X^{n-} = Cl^-$, $Br^-$, $SO_4^{2-}$, $NO_3^-$, DMSO, $NCS^-$
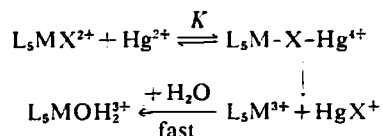
$M = Cr(III)$: $X^{n-} = Cl^-$, $Br^-$, $I^-$, $NCS^-$

The obtained results have been interpreted in the following manner: Firstly, a plot of $\Delta \bar{V}^{\neq}$ versus $\Delta \bar{V}$ for the various aquation reactions resulted in a linear relationship with a slope of approx. unity for $M = Co(III)$. This indicates that the transition state is in close agreement with the final (product) state, such that the leaving ligand $X^{n-}$ is almost fully dissociated. Secondly, evidence for a D mechanism was obtained from volume equation calculations[9,31] in which it turned out that a fairly constant volume of $54.9 \pm 0.9$ cm$^3$ mol$^{-1}$ can be calculated for the intermediate $Co(NH_3)_5^{3+}$ species according to the equation

$$\bar{V}\{Co(NH_3)_5^{3+}\} = \Delta \bar{V}^{\neq} - \bar{V}\{X^{n-}\} + \bar{V}\{Co(NH_3)_5X^{(3-n)+}\}$$

This is in good agreement with the partial molar volume of $55.1 \pm 1.1$ cm$^3$ mol$^{-1}$ for the Co-$(NH_3)_6^{3+}$ species, which is expected to be a good model for the former intermediate.[4] The latter comparison was recently criticized[66,67] since different partial molar volumes were found for some complex ions, and the exact nature of the discrepancy is at present further investigated. In another example[68] it was shown that for the aquation of a neutral ligand (urea), where $\Delta V_{solv}^{\neq}$ is expected to have a minor influence, a small positive $\Delta \bar{V}^{\neq}$ value was obtained, indicating the dissociative mechanistic character. For the reactions where $M = Cr(III)$, the $\Delta \bar{V}^{\neq}/\Delta \bar{V}$ plot resulted in a slope of $\sim 0.5$, which along with volume equation calculations was interpreted as evidence for an $I_d$ mechanism.

The interpretation of $\Delta \bar{V}^{\neq}$ for aquation reactions is sometimes complicated by the fact that $\Delta \bar{V}^{\neq}$ is small (positive or negative) and that the contribution from $\Delta V_{solv}^{\neq}$ is difficult to evaluate. An illustrative set of examples are the aquation reactions of $trans$-$CoN_xCl_2^+$ species, where $N_x = (NH_3)_4$: (en)$_2$; (Meen)$_2$: (Eten)$_2$; (Pren)$_2$: RS-(2.3.2. tet); RR, SS-(2.2. tet); (3.2.3. tet) and (cyclam), for which $\Delta \bar{V}^{\neq}$ values between $-3.1$ and $+1.0$ cm$^3$ mol$^{-1}$ were reported.[9,69] However, there are also examples in which $\Delta \bar{V}^{\neq}$ for aquation has a large negative ($viz.$, $-30$ cm$^3$ mol$^{-1}$ for $Ru(NH_3)_5Cl^{2+}$)[54] or a large positive value[71] ($viz.$, $24.5 \pm 0.3$ and $14.3 \pm 0.5$ cm$^3$ mol$^{-1}$ for $RhCl_6^{3-}$ and $RhCl_5(OH_2)^{2-}$, respectively; and between $7.8 \pm 0.5$ and $16.8 \pm 0.5$ cm$^3$ mol$^{-1}$ for $Co(CN)_5X^{3-}$, $X = Cl$, Br, I and $N_3$)[55] which are indicative of a purely associative (A) or dissociative (D) mechanism, respectively.

It is well known that aquation reactions of the type referred to above, can be catalyzed by metal ions, such as $Hg^{2+}$, according to the suggested general mechanism

$$L_5MX^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} L_5M-X-Hg^{4+}$$

$$L_5MOH_2^{3+} \overset{+H_2O}{\underset{fast}{\longleftarrow}} L_5M^{3+} + HgX^+$$

where $M = Co(III)$, Rh(III), Cr(III): $L = NH_3$ and $X = Cl$, Br, I.

For such a mechanism $\Delta \bar{V}^{\neq} = \Delta \bar{V}_K + \Delta \bar{V}_I^{\neq}$, such that $\Delta \bar{V}_I^{\neq}$ can only be obtained if $\Delta \bar{V}_K$ can

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Table 3. Volumes of activation for $Hg^{2+}$ assisted aquation reactions*

| Aquated Species | $\Delta \bar{V}^{*}$ | $\Delta \bar{V}_{K}$ cm³ mol⁻¹ | $\Delta \bar{V}_{k}^{*}$ | Reference |
|---|---|---|---|---|
| $Co(NH_3)_5Cl^{2+}$ | $-1.7 \pm 1.0$ | | | 71 |
| $Co(NH_3)_5Br^{2+}$ | $+0.8 \pm 0.5$ | | | 71 |
| $Cr(NH_3)_5Cl^{2+}$ | $+0.7 \pm 0.4$ | | | 71 |
| $Rh(NH_3)_5Cl^{2+}$ | $-1.0 \pm 0.4$ | | | 71 |
| $Rh(NH_3)_5I^{2+}$ | | $-1.7 \pm 1.0$ | $+1.2 \pm 0.3$ | 72 |
| $mer\text{-}RhCl_3(OH_2)_3$ | | $+2.8 \pm 0.3$ | $+8.1 \pm 0.4$ | 72 |

* Temperature in the range 11 to 25°C.

be estimated. The latter could only be measured in a few cases[72] (see Table 3), since in the remaining ones.[71] $K$ is very small and its pressure dependence cannot be measured directly or indirectly (*i. e.*, kinetically). It is obvious from the data in Table 3 that the reported volume quantities comprize contributions from both intrinsic and solvolytic sources as expected. which again makes the interpretation of the data rather uncertain.

The determination of $\Delta \bar{V}^{*}$ for aquation/solvolysis reactions of square planar complexes ($k_1$-path) has in general underlined the validity of the accepted associative reaction mode of the process. Typical results include $\Delta \bar{V}^{*}$ values between $-10.5$ and $-9.0$ cm³ mol⁻¹ for the aquation of Pt(dien)Cl⁺ and Pt(dien)Br⁺ at various ionic strengths ($10^{-2}$ to 1 M) and 25°C.[28] Similarly. $\Delta \bar{V}^{*} = -17 \pm 2$ and $-14 \pm 2$ cm³ mol⁻¹ for the aquation of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^{-}$, respectively.[73] For the reaction

$$Pd(Et_4 \text{ dien}) X^{(2-n)+} + H_2O \longrightarrow Pd(Et_4 dien) OH_2^{2+} + X^{n-},$$
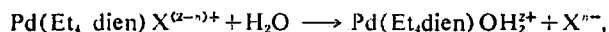
$\Delta \bar{V}^{*}$ values of $-14.9 \pm 0.2(X^{n-} = Cl^-)$, $-13.3 \pm 0.2(X^{n-} = Br^-)$. $-13.9 \pm 0.5(X^{n-} = N_3^-)$, $-11.5 \pm 0.2(X^{n-} = I^-)$, $-10.3 \pm 0.2(X^{n-} = NCS^-)$ and $-3.0 \pm 0.9(X^{n-} = NH_3)$ cm³ mol⁻¹ were reported.[61] A plot of $\Delta \bar{V}^{*}$ *versus* $\Delta \bar{V}$ yielded a straight line with a slope of $\simeq 0.5$, which was interpreted as evidence for an $I_a$ mechanism in which approx. 50% bond stretching occurs in the transition state. Volume equation calculations illustrated that a mean volume change of $-15.5 \pm 0.9$ cm³ mol⁻¹ represents the associative character of the reaction, which is close to the partial molar volume of the entering ligand, *i. e.*, water. $\Delta \bar{V}^{*}$ is furthermore expected to strongly depend on the nature of the solvent, as was illustrated for a number of systems.[63,74] Volumes of activation for the solvolysis of Pd(Et_4dien)I⁺ in various solvents at 40°C amount to $-12.9 \pm 0.4(EtOH)$. $-13.4 \pm 0.5(MeOH)$, $-11.5 \pm 0.2(H_2O)$, $-10.1 \pm 0.2(DMSO)$, $-9.3 \pm 0.3(DMF)$ and $-7.9 \pm 0.5(CH_3CN)$ cm³ mol⁻¹ and are in line with an $I_a$ mechanism. In one case[62,75] the values of $\Delta \bar{V}^{*}$ for the solvolysis of *cis*-Pt(PEt_3)_2(2, 4, 6-Me_3C_6H_2) Br in methanol (which are $-14.1 \pm 0.5$ and $-17.0 \pm 0.7$ cm³ mol⁻¹ at 30°C for the substitution by I⁻ and $SC(NH_2)_2$, respectively) provided direct evidence for an associative (A) mechanism and are in disagreement with the arguments presented by Romeo *et al.*,[76] in favor of a dissociative mechanism. These results led to a complete reinterpretation of the earlier reported data and

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Table 4.  Volumes of activation for the base hydrolysis of complexes of the
type $M(NH_3)_5X^{(3-n)+}$

| M | $X^{n-}$ | $\Delta V^{\neq}$ cm³ mol⁻¹ | $\Delta \beta^{\neq}$ cm³ mol⁻¹ kbar⁻¹ | Temp. °C | Reference |
|---|---|---|---|---|---|
| Co(III) | Br⁻ | + 8.5 | — | 25 | 77 |
| | SO₄²⁻ | +19.5 ± 1.1 | + 9.5 ± 2.2 | 15 | 4 |
| | SeO₃²⁻ | −17.1 ± 1.0 | −19 ± 2 | 25 | 4 |
| | PO₄³⁻ | +28.9 ± 2.2 | + 7.7 ± 2.1 | 55 | 4 |
| | Cl⁻ | +33.4 | — | 35 | 78 |
| Rh(III) | Cl⁻ | +18.7 ± 0.7 | — | 40 | 79 |
| | Br⁻ | +20.2 ± 0.5 | — | 40 | 79 |
| | I⁻ | +20.4 ± 0.5 | — | 40 | 79 |
| | NO₃⁻ | +22.3 ± 0.9 | — | 40 | 79 |

illustrate the diagnostic power of the high pressure kinetic technique.

The last type of substitution reaction to be discussed, is base hydrolysis. It is generally accepted that such reactions proceed by a dissociative conjugate base mechanism. For the pentaammine complexes these reactions consist of

$$M(NH_3)_5X^{(3-n)+} + OH^- \overset{K}{\rightleftharpoons} M(NH_3)_4(NH_2)X^{(2-n)+} + H_2O$$

$$\downarrow k$$

$$M(NH_3)_5OH^{2+} \overset{+H_2O}{\underset{fast}{\longleftarrow}} M(NH_3)_4(NH_2)^{2+} + X^{n-}$$
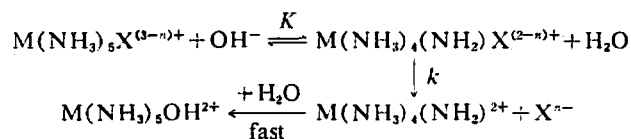
Some typical results are summarized in Table 4. For $X^{n-} = SeO_3^{2-}$ it was shown[4] that Se-O rather than Co-O bond breakage occurs during base hydrolysis, which results in a large increase in solvation and therefore decrease in $\Delta V^{\neq}$ and $\Delta \beta^{\neq}$ in comparison to the other systems. Furthermore it must be kept in mind that $\Delta V^{\neq}$ is once again a composite value, i.e., $\Delta V^{\neq} = \Delta V_K + \Delta V_k^{\neq}$. Stranks[4] estimated $\Delta V_K$ to be +18 cm³ mol⁻¹, such that $\Delta V_k^{\neq}$ is negative ($\sim -10$ cm³ mol⁻¹) for the hydrolysis of $Co(NH_3)_5Br^{2+}$ and in good agreement with $\Delta V^{\neq}$ for the aquation[29] of this complex. On the other hand, $\Delta V_k^{\neq}$ is zero or positive for the remaining Co(III) complexes (Table 4), suggesting that these hydrolysis reactions may have some dissociative character.[4] In the case of the Rh(III) species,[79] volume equation calculations seem to favour an $I_d$, instead of D, type of mechanism.

As a final comment concerning the interpretation of $\Delta V^{\neq}$ for substitution reactions of inorganic complexes, we would like to point to a recent comment made by Langford[80] in which he underlines the role played by the nonlabile ligands. This may indeed be of importance, however no study has so far been made of the influence of non-reacting ligands. We support the general arguments of Swaddle[81] that $\Delta V^{\neq}$ can only in part be ascribed to changes in the bond distances of non-reacting ligands. Furthermore, we want to emphasize that $\Delta V^{\neq}$ can surely, not be used as the only mechanistic probe. The discussion of mechanisms should also rely on other kinetic and chemical information, aspects which have not been

included in the present paper.

### 4-2.  *Isomerization reactions*

Three different types of isomerization reactions of inorganic compounds will be discussed. *viz.*, racemization. geometrical and linkage isomerization.  Recent reviews[8,3] have discussed these reactions in detail. such that we can focus on a number of typical illustrative examples.

Various mechanisms have been proposed for racemization reactions of octahedral complexes. These include an intermolecular mechanism in which complete loss of one chelate occurs, and two different types of intramolecular processes.  One proceeds *via* dechelation to produce a five-coordinate intermediate. and the other *via* a twist mechanism without bond rupture (see Fig. 4).  Overall volume changes ($\Delta \bar V$) for such reactions are zero, and $\Delta \bar V^{*}$ (for which a number of examples are given in Table 5) can usually be interpreted according to the above mentioned mechanisms.

The volume of activation for the racemization of $Fe(phen)_3^{2+}$ is in good agreement with that reported for the aquation process, which favours a dissociative mechanism.  However, due to a meaningfull difference in the rates of these processes. this interpretation is questionable and



intermolecular dissociation

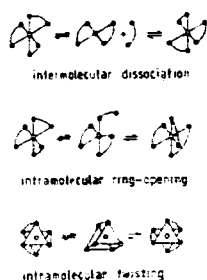intramolecular ring-opening

intramolecular twisting

Fig. 4.  Schematic representation of different racemization mechanisms of octahedral species,

Table 5.  Volumes of activation for some typical racemization reactions

| Reactant[a] | [HCl] M | Temp. °C | $\Delta \bar V^{*}$ cm³ mol⁻¹ | Reference |
|---|---|---|---|---|
| $Fe(phen)_3^{2+}$ | 0.01 | 25 | $+14.2 \pm 0.3$ | 8, 82 |
|  | 1.0 | 25 | $+15.6 \pm 0.3$ |  |
| $Ni(phen)_3^{2+}$ | 0.01 | 45 | $-0.4 \pm 0.2$ | 8, 82 |
|  | 1.0 | 45 | $-1.5 \pm 0.3$ |  |
| $Cr(phen)_3^{3+}$ | 0.05 | 75 | $+3.3 \pm 0.3$ | 8. 83 |
| $Cr(bpy)_3^{3+}$ | 0.05 | 75 | $+3.0 \pm 0.3$ |  |
| $Cr(ox)_3^{3-}$ | 0.05 | 15 | $-16.3 \pm 0.4$ |  |
| $Cr(ox)_2(phen)^-$ | 0.05 | 25 | $-12.3 \pm 0.3$ |  |
| $Cr(ox)_2(bpy)^-$ | 0.05 | 25 | $-12.0 \pm 0.3$ |  |
| $Cr(ox)(phen)_2^+$ | 0.05 | 45 | $-1.5 \pm 0.3$ |  |
| $Cr(ox)(bpy)_2^+$ | 0.05 | 45 | $-1.0 \pm 0.2$ |  |

[a] phen = 1. 10-phenanthroline,
bpy  = 2, 2'-bipyridyl,
$ox^{2-}$ = oxalate.

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arguments in favour of a twist mechanism have been given.[83] In contrast, a good agreement in the $\Delta V^{\neq}$ values and rate constants is found in the case of $Ni(phen)_3^{2+}$, which is in line with an intermolecular dissociative mechanism. The reported $\Delta V^{\neq}$ values for $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$ are almost equal and considered as evidence for an intramolecular twist mechanism. The large negative $\Delta V^{\neq}$ values for $Cr(ox)_3^{3-}$, $Cr(ox)_2(phen)^-$ and $Cr(ox)_2(bpy)^-$ point towards an intramolecular one-ended dissociation for which a theoretical $\Delta V^{\neq}$ of $-10$ cm$^3$ mol$^{-1}$ is expected.[83] The last two entries in Table 5 are once again indicative of a twist mechanism.

Mechanisms similar to those described above can lead to geometrical isomerization. These include[6]: one-ended dissociation of a bidentate ligand; dissociation of a unidentate ligand; twisting without bond rupture; and an associative reaction with a nucleophile. Extreme values for $\Delta V_{intr}^{\neq}$ of $+15$ and $-15$ cm$^3$ mol$^{-1}$ are expected[6] for isomerization via the dissociative release and the associative entrance of an aquo ligand, respectively. For the trans-cis isomerization of $Co(en)_2(OH_2)_2^{3+}$, $\Delta V^{\neq}=14.3\pm0.2$ cm$^3$ mol$^{-1}(35°C, [H^+]=0.05$ M),[84] which is compatible with the dissociative release of an aquo ligand. $\Delta V^{\neq}$ values between $+7.3\pm0.2$ and $+7.9\pm0.3$ cm$^3$ mol$^{-1}$ were reported[4,85,86] for the isomerization of trans-$Co(en)_2(OH_2)X^{n+}(X=SeO_3H^-$, $SeO_3^{2-}$ and $CH_3COO^-$) and also confirm such a mechanism. In contrast to these values, $\Delta V^{\neq}=-16.6\pm0.5$ cm$^3$ mol$^{-1}$ for the isomerization of trans-$Cr(C_2O_4)_2(OH_2)_2^-$ and is consistent with the one-ended dissociation of a chelated oxalate ligand.[87] The large negative $\Delta V^{\neq}$ value originates mainly from the increase in electrostriction due to charge creation during the ring-opening process. In the presence of $HClO_4$ the $\Delta V^{\neq}$ value decreases to $-5.4\pm1.0$ cm$^3$ mol$^{-1}$ and the difference is ascribed[88] to the protonation of the mono-dentate ligand. On the other hand, $\Delta V^{\neq}$ for the isomerization of trans-$Cr(CH_2C_2O_4)_2(OH_2)_2^-$ is $+8.9\pm0.3$ cm$^3$ mol$^{-1}$ and the release of an aquo ligand is suggested in this case.[87]

The measurement of $\Delta V^{\neq}$ has led to a better understanding of the geometrical isomerization of sterically hindered complexes of the type cis-$Pt(PEt_3)_2(R)X$, where $R=C_6H_5$, $p$-$MeC_6H_4$, $o$-$MeC_6H_4$, $o$-$EtC_6H_4$, 2, 4, 6-$Me_3C_6H_2$, and $X=Cl$, Br. These reactions were suggested.[76,89,90] to proceed via a dissociative mechanism (Scheme I-Fig. 5) in which a three-coordinate intermediate is produced. Since the isomerization and solvolysis reactions of the most sterically hindered complex of the series, viz., R=mesityl, were reported to be identical in rate and activation parameters, the arguments were extended[76] to suggest a dissociative solvolysis mechanism in this case. However, $\Delta V^{\neq}$ for the latter reactions were found[62,91] to be $-12.0$ $\pm0.5$ and $-14.1\pm0.5$ cm$^3$ mol$^{-1}$, respectively, which could only be interpreted in terms of an
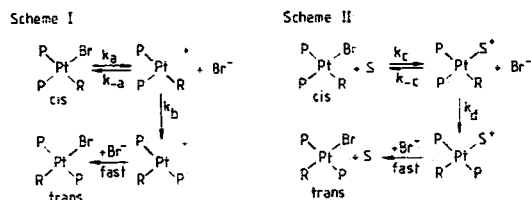


Fig. 5, Schematic representation of the isomerization mechanisms of cis-$Pt(PEt_3)_2(R)Br$.

associative solvolysis mechanism (Scheme II–Fig. 5). It was further suggested,[62,91] that the difference in activation parameters for isomerization and solvolysis of the less sterically hindered complexes, $i.e.$, all R excluding R=mesityl, is due to a switch in rate-determining step within the mechanism[62,75] (Scheme II–Fig. 5), rather than due to a switch in the nature of the mechanism.[76,89,91,92]   Under steady state conditions
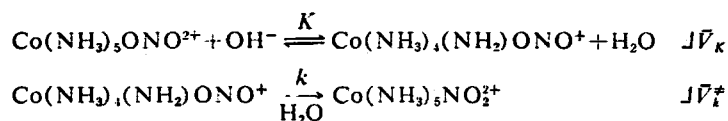
$$k_{obs} = k_c k_d / \{k_{-c}[Br^-] + k_d\}$$

and $k_{obs} = k_c$ in the absence of added Br⁻. If the first step is a rapid pre-equilibrium, $i.e.$, $k_c$ and $k_{-c} \gg k_d$, then

$$k_{obs} = K_c k_d / \{[Br^-] + K_c\}, \quad K_c = k_c / k_{-c}$$

and $k_{obs} = k_d$ in the absence of added Br⁻. It follows that a switch in rate-determining step ($k_c$ to $k_d$) can occur depending on the magnitudes of the various rate constants, which in turn depend on the influence of R. It therefore turns out that $k_c$ is the rate-determining step for R=mesityl, and $k_d$ for all the other less sterically hindered substituents (R). This is also observed in the $\Delta V^*$ values since it was found[91,93] that $\Delta V^* = +6.4 \pm 0.4$, $+5.2 \pm 0.3$ and $+7.2 \pm 0.8$ cm³ mol⁻¹ for the isomerization of $cis$-Pt(PEt₃)₂(C₆H₅)X where X=Cl, Br and I, respectively, $i.e.$, the $k_d$-reaction. The exact nature of this process is still uncertain,[93] although pseudo rotation of a five-coordinate intermediate followed by a rate–determining dissociative step to yield the four-coordinate $trans$ product, is a possible mechanism.

Activation volumes for the linkage isomerization reactions of complexes of the type M(NH₃)₅ONO²⁺ in aqueous solution were reported[94] to be $-6.7 \pm 0.4$, $-7.4 \pm 0.4$ and $-5.9 \pm 0.6$ cm³ mol⁻¹ for M=Co(III), Rh(III) and Ir(III), respectively. These values support the idea of a common intramolecular rearrangement of the nitrito ligand, and is in agreement with earlier observations.[95,96]   Recently Sargeson and co-workers[97] reported that these isomerization reactions are catalyzed by OH⁻. They found a $\Delta V^*$ value of $+27 \pm 1.4$ cm³ mol⁻¹ for the base-catalyzed linkage isomerization of Co(NH₃)₅ONO²⁺, which was rationalized in terms of a conjugate base pre-equilibrium mechanism:

$$Co(NH_3)_5ONO^{2+} + OH^- \xrightleftharpoons{K} Co(NH_3)_4(NH_2)ONO^+ + H_2O \quad \Delta \bar{V}_K$$

$$Co(NH_3)_4(NH_2)ONO^+ \xrightarrow[H_2O]{k} Co(NH_3)_5NO_2^{2+} \quad\quad\quad \Delta \bar{V}_I^*$$

$\Delta \bar{V}_K$ is expected to be between $+18$ and $+22$ cm³ mol⁻¹ due to the unusually large volume of electrostriction of the hydroxide ion, such that a value of at least $+5$ cm³ mol⁻¹ can be assigned to $\Delta \bar{V}_I^*$.

The volume of activation for the linkage isomerization of Co(NH₃)₅SCN²⁺ was reported to be $-5.3 \pm 0.8$ cm³ mol⁻¹ in water and $-1.0 \pm 1.2$ cm³ mol⁻¹ in DMSO.[98] Although this reaction was shown to be an intramolecular process,[99] the $\Delta V^*$ values are not in agreement with a mechanism which involves M–S bond cleavage and the subsequent formation of an "intimate ion-pair", since this would lead to a positive $\Delta V^*$. The magnitude of $\Delta V^*$ also

complicates its interpretation in these cases. In contrast, the mechanism for the linkage isomerization of $Pd(Et_4 dien)SCN^+$ seems to be the same as that for solvolysis. $\Delta V^{\neq}$ was found[100] to be $-10.8 \pm 0.3$ and $-10.6 \pm 0.4$ cm$^3$ mol$^{-1}$ for these reactions, respectively. Similarly, values of $-9.5 \pm 0.5$ and $-10.5 \pm 0.6$ cm$^3$ mol$^{-1}$ were reported[100] for the corresponding reactions of the sterically more crowded complex $Pd(MeEt_4 dien)SCN^+$.

### 4-3. *Redox reactions*

Redox reactions of inorganic complexes can generally be described in terms of an outer-sphere or an inner-sphere mechanism. In the first, electron transfer occurs without bond-making or -breaking, and Stranks[4] has succeeded to predict the volume of activation for such reactions based on the theories of Marcus and Hush. The systems $Co(en)_3^{2+}/Co(en)_3^{3+}$ for which $\Delta V^{\neq} = -19.8 \pm 1.5$ (experimental) and $-18.4$ (theoretical) cm$^3$ mol$^{-1}$, and $Fe(OH_2)_6^{2+}/Fe(OH_2)_6^{3+}$ for which $\Delta V^{\neq} = -12.2 \pm 1.5$ (experimental) and $-14.4$ (theoretical) cm$^3$ mol$^{-1}$ may serve as typical examples. In contrast, the observed $\Delta V^{\neq}$ values for the reactions between $Fe(OH_2)_5OH^{2+}$ and $Fe(OH_2)_6^{2+}$, and $Cr(OH_2)_5OH^{2+}$ and $Cr(OH_2)_6^{2+}$ were found[4] to be $-0.4 \pm 0.4$ and $+4.2 \pm 1.1$ cm$^3$ mol$^{-1}$, respectively. The latter values are significantly more positive than the values $-11.4$ and $-11.6$ cm$^3$ mol$^{-1}$, respectively, predicted for an outer-sphere mechanism. They indicate that the hydroxo species react by an inner-sphere mechanism in which a bridged species is produced in the transition state. The excess positive $\Delta V^{\neq}$ values are ascribed to the dissociative release of one aquo ligand during the formation of the transition state.

Candlin and Halpern[101] studied the system $Co(NH_3)_5X^{2+}/Fe^{2+}$ and found $\Delta V^{\neq}$ values of $+11(X=F)$, $+8(X=Cl, Br)$ and $+14(X=N_3)$ cm$^3$ mol$^{-1}$, which are once again substantially more positive than the theoretically expected values[4] ranging between $-10.6$ and $-12.8$ cm$^3$ mol$^{-1}$ for an outer-sphere mechanism. Again it is suggested that the mechanism must be of the inner-sphere type in which the release of water in the transition state overcomes the opposing negative volume effects originating from solvent electrostriction. The exact nature of the mechanism is, however, still under discussion due to some interesting results reported[102-105] for these reactions in dipolar aprotic solvents (DMSO and DMF). In addition, high pressure studies in DMSO[106] resulted in $\Delta V^{\neq}$ values of $10.3 \pm 0.4(X=F)$, $3.8 \pm 0.7(X=Cl)$ and $0.0 \pm 0.4(X=Br)$ cm$^3$ mol$^{-1}$, which seem to parallel the corresponding values for the reactions in aqueous medium. The reasons for the observed deviations in $\Delta V^{\neq}$ are rather uncertain and probably due to solvational effects and steric crowding at the bridging site. The mechanism involved is probably more complex[106] than the oversimplified model described by an inner- and outer-sphere mechanism.

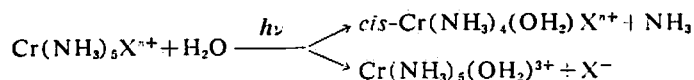### 4-4. *Photochemical substitution reactions*

Photochemical redox and substitution reactions of inorganic complexes have been studied by numerous groups in the past. The emphasis was usually placed on the identification of

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Table 6.  Apparent volumes of activation for photo-aquation reactions of some cationic Cr(III) complexes[107]

| Complex | $\Delta \bar{V}_{app}^{\neq}$, cm³ mol⁻¹ | |
|---|---|---|
| | Substitution of $NH_3$ | Substitution of X |
| $Cr(NH_3)_5Cl^{2+}$ | $-6.0 \pm 0.4$ | $-13.0 \pm 0.5$ |
| $Cr(NH_3)_5Br^{2+}$ | $-6.5 \pm 0.1$ | $-12.2 \pm 0.3$ |
| $Cr(NH_3)_5NCS^{2+}$ | $-6.4 \pm 0.1$ | $-9.8 \pm 0.2$ |
| $Cr(NH_3)_6^{3+}$ | $-6.7 \pm 0.5$ | — |

intermediates and photolysis products, the determination of quantum yields and the description of the photo-excited states.  Until recently, no effort had been made to study the pressure dependence of such reactions in order to obtain insight into the molecular nature (dissociative or associative character) of the photoreactions.

The first of these studies[107] concerned the ligand field photolysis of some cationic Cr(III) ammine complexes:

$$Cr(NH_3)_5X^{n+}+H_2O \xrightarrow{h\nu} \begin{array}{l} cis\text{-}Cr(NH_3)_4(OH_2)X^{n+}+NH_3 \\ Cr(NH_3)_5(OH_2)^{3+}+X^- \end{array}$$

$n=2$: X=Cl, Br, NCS; $n=3$: X=NH$_3$.

In this system the loss of $NH_3$ is the predominant photoreaction, whereas the loss of $X^-$ occurs to a much smaller extent and in addition is the only observable thermal reaction.  Although quantum yield is a composite of the rate constants for the primary photochemical reaction and the photophysical deactivating processes. recent measurements[108] indicated that the latter process is almost pressure independent.  Thus the pressure dependence of the quantum yield can be related to that of the primary photochemical process.  The apparent volumes of activation ($\Delta \bar{V}_{app}^{\neq}$) for the investigated reactions were estimated from the pressure dependence of the measured quantum yields. and the obtained results are summarized in Table 6.  The values of $\Delta \bar{V}_{app}^{\neq}$ for the photo-substitution of X are in close agreement with those reported for the corresponding thermal reactions[64,65] (see earlier discussion)  and are also considered as evidence for an $I_a$ mechanism.   Similarly. the almost constant and negative values of $\Delta \bar{V}_{app}^{\neq}$ for the photo-substitution of $NH_3$ confirm an $I_a$ type of mechanism.   Detailed volume equation calculations were performed[107] to illustrate the validity of these conclusions.

In a follow-up study[109] the pressure dependence of the photo-aquation reactions of anionic Cr(III) and Co(III) complexes was determined.  $\Delta \bar{V}_{app}^{\neq}$ turned out to be $+2.1\pm0.4$. $+2.7\pm 0.2$ and $+1.3\pm0.1$ cm³ mol⁻¹ for the photo-aquation of $Cr(NCS)_6^{3-}$, $Cr(CN)_6^{3-}$ and $Co(CN)_6^{3-}$, respectively.  These data support an $I_d$ type of mechanism in all cases.

## 5.  Concluding Remarks

The numerous examples discussed in the preceeding sections illustrate the progress that has

been made in recent years in the elucidation of inorganic reaction mechanisms by using high pressure techniques. The problems experienced by researchers in this field to unequivocally interpret some of their results, are largely due to the lack of data for similar or closely related systems.

Certainly the obtained characteristic data for the volumes of activation and reaction as well as the partial molar volumes of reactants and products should be supplemented by other kinetic and thermodynamic parameters such as rate constants, activation enthalpies and entropies, reaction enthalpies *etc.* in order to reach a complete understanding of the mechanisms.

Major problems in the interpretation of $\Delta \bar{V}^{\neq}$ values still remain to be solved. These include for instance the uncertainties in the estimation of $\Delta V_{solv}^{\neq}$, the often unknown temperature and ionic strength dependencies of $\Delta \bar{V}^{\neq}$, and the complications introduced by the more complex mechanisms. More information is required on the physical meaning of the pressure dependencies of $\Delta \bar{V}^{\neq}$.

Since there is an increasing interest in high pressure kinetics, it is hoped that some of these problems can be solved as more data become available.

## Acknowledgements

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