

The interpretation and mechanistic significance of activation volumes for organometallic reactions

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- 1 Introduction: basic principles and theory 1
 - 2 Experimental 5
 - General considerations 5
 - Conventional time-range reactions 6
 - Rapid reactions 10
 - Radiation-induced reactions 12
 - Electrochemical methods 16
 - NMR spectroscopy 16
 - Partial molar volumes from density measurements 18
 - Miscellaneous topics 18
 - 3 Volumes of activation for thermal organometallic reactions 22
 - Solvent exchange 23
 - Ligand substitution 26
 - Isomerisation reactions 49
 - Redox reactions 50
 - Oxidative addition and reductive elimination reactions 52
 - Reactions of small molecules 55
 - Addition reactions 57
 - Other reactions 59
 - 4 Volumes of activation for radiation-induced organometallic reactions 63
 - Photo-induced reactions 63
 - Pulse-radiolysis-induced reactions 66
 - 5 Concluding remarks 69
- Acknowledgements 69
References 69

1 Introduction: basic principles and theory

An initial effort to understand the effect of hydrostatic pressure on reaction rates was presented at the beginning of the last century.¹ The argument could be developed from the thermodynamic relationship between the volume change for a reaction, ΔV , the change in Gibbs free energy (ΔG) for the reaction, and the hydrostatic pressure, P . Since:

$$V = (\delta G / \delta P)_T \quad (1)$$

therefore:

$$\Delta V = (\delta \Delta G / \delta P)_T \quad (2)$$

Since:

$$\Delta G = -RT \ln K \quad (3)$$

in which K is the equilibrium constant for the reaction, R is the ideal gas constant and T is the absolute temperature:

$$(\delta \ln K / \delta P)_T = -\Delta V / RT \quad (4)$$

To generate an expression for the effect of pressure upon equilibria and extend it to reaction rates, this early work consisted of drawing an analogy with the effect of temperature on reaction rates embodied in the Arrhenius equation of the late 19th century.² In the more coherent understanding since the development of transition state theory (TST),³⁻⁶ the difference between the partial molar volumes of the transition state and the reactant state is defined as the volume of activation, ΔV_f^\ddagger , for the forward reaction. A corresponding term ΔV_r^\ddagger applies for the reverse reaction. Throughout this contribution ΔV^\ddagger will be used and is assumed to refer to the forward reaction unless an equilibrium is under discussion. Thus:

$$\Delta V = \Delta V_f^\ddagger - \Delta V_r^\ddagger \quad (5)$$

These parameters can be displayed as a volume profile for a reaction to complement other thermodynamic parameter profiles of free energy, enthalpy and entropy. It is also possible in certain circumstances, discussed below, to place the volume profile on an absolute scale rather than only on a relative volume scale.

Assuming for the moment that the volume parameters can be obtained from experimental practice, an important question is what do the numerical values signify, and furthermore what changes in molecular species are occurring giving rise to a volume change? In other words is there a quantitative framework of interpretation of volume parameters? It was discerned that partial molar volume changes consist primarily of two components.^{7,8} The first results from volume changes of the molecular species themselves, e.g. bond breakage or bond formation (complete or partial), isomerisation or bond deformation. When intrinsic changes give rise to an increase or decrease in polarity or charge development or charge neutralisation in species the second component manifests itself in solvation changes. In the presence of a charged species surrounding solvent molecules are reduced in their molecular volume, an effect termed electrostriction. Hence an increase or decrease in polarity or charge causes a change in the extent of electrostriction. Thus:

$$\Delta V = \Delta V_{\text{intr}} + \Delta V_{\text{solv}} \quad (6)$$

and

$$\Delta V^\ddagger = \Delta V_{\text{intr}}^\ddagger + \Delta V_{\text{solv}}^\ddagger \quad (7)$$

If a volume parameter can be determined with reasonable precision, the mechanistic features of the reaction can be assessed, and set in the context of the magnitude of a given volume parameter. This is not necessarily a straightforward process and guidelines have been developed for intrinsic mechanistic features based on compilations of volume parameters assembled in the literature.⁹⁻¹² In general, except

for related series of reactions, each system must be examined and analysed based on its own characteristics and the underlying chemistry.

Historically, determination of volumes of activation was more prevalent in organic chemistry and early work also considered the possible relationship between the volume of activation and the entropy of activation.^{9,13} In the past several decades growth in the incidence of reports of determination of activation volumes of inorganic reactions, particularly those of coordination compounds, has greatly increased.^{12,14-16} Bioinorganic chemistry has witnessed an increase in the application of the volume of activation as a mechanistic indicator.¹⁶ Organometallic chemistry, one important aspect of which is the use of metal complexes in activation of organic molecules to promote conversion of them into other (more useful) molecules and related catalytic cycles, has blossomed as a field of endeavour. This is evident since several journals are dedicated to reports of organometallic synthetic and reaction chemistry. Furthermore comprehensive series have appeared¹⁷ and organometallic chemistry is frequently presented in prestigious journals since many organometallic reactions have beside their intrinsic interest significant industrial relevance and economic impact. Consequently, mechanistic studies have assumed considerable importance for understanding individual steps within overall catalytic cycles. Successful elucidation of the reaction mechanism permits modification and tuning of reaction systems to improve yields or efficiency. Of various experimental variables that may be explored, e.g. concentration, ionic strength in appropriate media, electrolyte, solvent, substituents, isotopic substitution and temperature, the variation of hydrostatic pressure leading to the volume of activation can often provide decisive mechanistic information.¹⁸

The purpose of this contribution is to illustrate the value and significance of volumes of activation in a wide range of organometallic chemistry reactions. This will follow an outline of basic experimental design and the methods and experimental practice in determining volumes of activation.

Upon modifying Equation (4) to be applicable to the equilibrium between the transition state and the reactant state from TST, the equation that can be applied to experimental kinetic data (rate constants, k_p at various pressures) is developed:

$$(\delta \ln k_p / \delta P)_T = -\Delta V^\ddagger / RT \quad (8)$$

The integrated form:

$$\ln k_p = \ln k_0 - (\Delta V^\ddagger / RT)P \quad (9)$$

may be used to obtain the volume of activation by plotting $\ln k_p$ versus P , where k_0 is the value of the rate constant at zero pressure. In fact the latter parameter is always very close to the value of the rate constant at atmospheric pressure. If such a plot is linear, the volume of activation is readily obtained from the slope. This is nearly always the case for pressures in the range 0–150 MPa (1 atm = 1.01325×10^5 Pa). When the volume of activation is not independent of pressure and the plot is non-linear, there are various treatments of the data that allow extraction of the volume of activation.¹⁹⁻²² In addition there are reviews²³ and mathematical treatments from a thermodynamics standpoint²⁴ of the physicochemical effects of

pressure. The dependence of ΔV^\ddagger on pressure is characterised by the term $\Delta\beta^\ddagger$, the compressibility of activation. When required the compressibility of activation could be obtained by extending the pressure range of kinetics measurements. However, this can increase the technical specifications of apparatus, and is often not necessary. The dependence on pressure of the volume of activation arises mostly when the properties of the solvent are significantly affected by increasing pressure, giving rise to a second effect upon the pressure variation of the rate constant. This latter effect is normally small for aqueous media and is more likely to manifest itself when a reaction is conducted in an organic solvent. While the dependence on pressure of the volume of activation is of considerable interest, particularly from the point of view of the effect of pressure on solvent properties, this aspect will not be treated further here. Nevertheless the effect of pressure on solvent properties, e.g. upon the melting point (m.p.), must be considered in experimental design: the m.p. of benzene at atmospheric pressure is 5.5°C and is about 100°C at 500 MPa, whereas water has an m.p. of -9°C at 100 MPa.²⁵ Other factors that need to be addressed in aqueous solutions are the effect of pressure on the ion-product constant for water, thus affecting the pH scale, and the effect of pressure on the $\text{p}K_a$ values of weak acids and $\text{p}K_b$ values of weak bases. In addition to the effects of pressure on the compressibility and the m.p. of a solvent, the boiling point, viscosity, density, dielectric constant and conductivity are also affected by pressure and cognisance of these effects must be undertaken when relevant in design of experiments.

When the rate constant is increased by increasing pressure, ΔV^\ddagger is negative, and conversely when the rate constant is decreased by increasing pressure, ΔV^\ddagger is positive. Why are pressures up to 150 MPa typically used? It will be shown from typical values of ΔV^\ddagger that a smaller range would not normally be adequate to establish ΔV^\ddagger with sufficient precision for mechanistic diagnosis.

Obviously, if the rate law is complex so that activation parameters obtained are composites of several terms then interpretation becomes more difficult as the experimentally acquired volume of activation needs to be appropriately apportioned. However, in some cases varying the experimental conditions, concentrations for example, a complex rate law can be reduced to a simpler form with attendant lowering of interpretation difficulties.

It is clear that from the integrated form of Equation (4) the volume of reaction can be obtained if the equilibrium constant can be determined over a range of pressure. If the volume of activation is not experimentally accessible for one of the directions of the reaction, ΔV can be used to calculate its value. Under certain conditions and with suitable properties of reactants and/or products it may be possible to determine their partial molar volumes, hence allowing development of a volume profile on an absolute volume basis, as noted above. Even if ΔV can be determined either from the pressure dependence of the equilibrium constant and/or from use of Equation (5), it may be possible to confirm its value by determination of the partial molar volumes from density measurements. The conditions for conducting successful determinations of partial molar volumes are rather stringent and will be described in Section 2. The method depends on measuring the density, d , of several solutions of different concentrations of the reactant or product. The following equation is used to obtain

the apparent molar volume, ϕ at each molar concentration, c :

$$\phi = (\text{MW}/d) - ((d - d_0)/d_0) \times (1000)/c \quad (10)$$

The density of the solvent is d_0 and MW is the molar mass of the solute. The values of the apparent molar volume are plotted against concentration and the partial molar volume is the value obtained by extrapolation to zero concentration.

2 Experimental

GENERAL CONSIDERATIONS

The methods, techniques, apparatus and instruments relating to determination of volumes of activation for organic, inorganic and bioinorganic reactions, in most cases, can be applied in organometallic chemistry. Several publications have covered the practical aspects of determining kinetic parameters at elevated pressures.^{16,26-33} These should be consulted for complete details, and they also illustrate the history and development of methodology in high pressure chemistry kinetics practice. Determination of rate constants from kinetic data at ambient pressure has been described in several authoritative works.^{6,34-40} The processing of kinetic data to obtain kinetic parameters at high hydrostatic pressures is usually essentially no different. The emphasis here will be on the techniques of high pressure practice and the apparatus and equipment that are required. A system (e.g. type of instrument and monitoring method) that is suitable for following the kinetics at ambient pressure requires adaptation or modification for use at elevated pressures. The actual application of pressure is by standard arrangements of pumps with appropriately placed high pressure rated valves: these aspects will not be emphasised here, and literature that provides both more information and further sources may be consulted. Pressure measurement is either by a Bourdon-type gauge or a pressure transducer. Since small increments or decrements of pressure cause almost negligible changes in rate, pressure measurements to an accuracy of 1-2% or less are acceptable.

There are many organometallic reactions requiring the presence of one or more gases in the reacting solution and in equilibrium with the same gases above the solution. The pressure of the gas is often subject to variation, but this is for the purpose of improving synthetic yield or for improving catalytic efficiency. The pressures involved are usually well below those of hydrostatic pressures applied in the volume parameter determination and these experiments do not result in obtaining volumes of activation. While such reactions are extremely important in the context of using metal complexes in organic transformations with gases under pressure, they will not be included here. However, reference may be made to some key sources,⁴¹⁻⁴⁴ particularly as some of these studies make use of very specialised instrumentation.

The design and construction of high pressure containers or cells depend on the monitoring method and whether the reaction may be classified as conventional in its time range or is a fast reaction. The division between the two is not defined and in

some cases is somewhat different from the division at ambient pressure. If the reactants are mixed at ambient pressure, monitoring of reaction progress can commence as soon as the monitoring process operates, providing the reactants have been thermally equilibrated in advance. Upon pressure application to the mixed reactants the temperature of the system increases quite rapidly. The extent depends on the magnitude of pressure and on the heat capacity of the solvent. Aqueous media are less affected by heating under compression. Nevertheless the time of restoration to the temperature of kinetics measurement means that conventional time range involves reactions having half-lives of the order of 10 min for high pressure reactions rather than a few to several seconds for ambient pressure experiments. Obviating this problem can be accomplished in some cases by the simple expedients of either studying the reaction kinetics at a much lower temperature or in the case of second-order reactions diluting the reactants.

CONVENTIONAL TIME-RANGE REACTIONS

For reactions that are slow at room temperature, one approach is to initiate reaction and confine the reaction to an autoclave. Following decompression the contents can be analysed to assess the progress of the reaction. This procedure was used to determine the first volume of activation for an inorganic reaction. Apparently only one elevated pressure was used to estimate the value.⁴⁴ In more current practice repeating the process and arresting the reaction at different time intervals could lead to a reaction profile at a given pressure. The whole procedure would then be repeated at several different pressures, and kinetic data treated according to Equation (9). Obviously such a primitive method is to be avoided, as it is very labour intensive and wasteful of reactants. It would only be satisfactory if the analysis is very rapid compared with the reaction rate or the reaction can be quenched immediately upon decompression.

An extension of this method would allow periodic aliquot sampling from a container whose contents are subjected to high pressure. Obvious conditions govern whether this method would be satisfactory. They are as follows:

- (1) The reaction progress must be very slow relative to the time required for aliquot removal and time of sample analysis, or in the latter case a rapid quench can be carried out. A rapid analytical method is UV/visible spectrophotometry.
- (2) Pressure restoration inside the container following each sample removal must be very rapid compared with the rate of reaction.
- (3) The reaction rate must be slow so that the half-life of reaction is much longer than the time required for sample introduction into and sealing of the pressure vessel, and for thermal equilibration following heating of the sample caused by compression, as noted above.

Sample overheating can be avoided by stepwise pressure application. For this type of pressure apparatus the container must be sufficiently robust to withstand high

pressures. If the material is steel or other metal alloy an inert inner coating may be required if the sample contains metal coordinating or particularly chelating ligands with high stability constants for metal complex formation. This in turn may cause a sealing problem as the aliquot sampling method depends on successful operation of a piston, usually of Teflon with one or more "O" rings that move to compensate for the volume change upon each sample removal. A piston-cylinder apparatus has been widely used and volumes of activation determined. Most reports are of substitution reactions⁴⁵⁻⁴⁹ and one of electron transfer of transition metal complexes.⁵⁰ The method has also been used for organometallic reactions.^{51,52} A representative sample apparatus is schematically shown in Fig. 1.

A much more efficient method of obtaining kinetic parameters involves continuous monitoring of the reaction sample while it is subject to hydrostatic pressure, i.e. an *in situ* sampling method. This necessitates construction of a pressurisable sample container that can be incorporated within the observation housing of an instrument. The preferred option is to modify a commercial instrument, although this may have the drawback of requiring dedication of the instrument to the high pressure mode. Interchange between high pressure and ambient pressure modes may be a time-consuming exercise. There are two approaches that can be described for the most

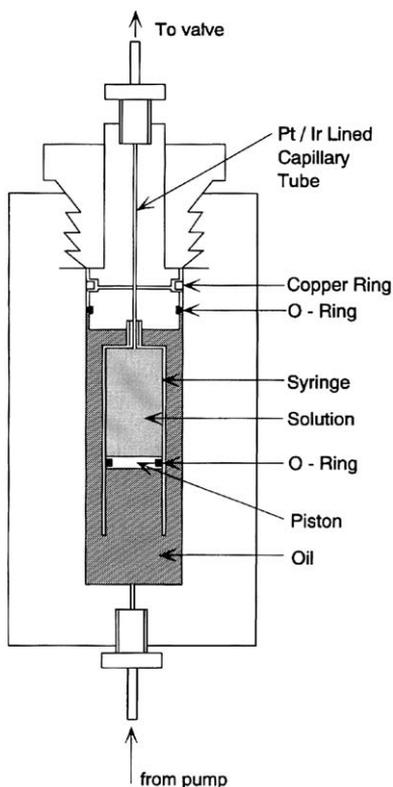


Fig. 1 An example of a piston-cylinder high pressure apparatus.

frequently applied monitoring method, UV/visible spectrophotometry. One uses a pressurisable cuvette that is aligned with the light path of a spectrophotometer, and the cuvette is held in place by a metal block, also possessing optical windows. The metal block contains thermostatted external circulating fluid and optically transparent pressurisable fluid surrounding the cuvette. The cuvette is typically of the “pill-box” type, designed several decades earlier.⁵³ The pill-box cuvette is cylindrical with two concentric cylinders that can be rotated for sealing after filling with a reacting sample. Incident and transmitted light pass through the optically flat circular end windows. The design allows for path length reduction upon compression of the contents by the surrounding compressed fluid, usually, *n*-heptane. A schematic diagram of a pill-box cell and its enclosing pressurisable container is shown in Fig. 2.

A second variant uses a metal block containing a machined out cuvette and windows that is placed in the cell compartment of a spectrophotometer. The pressure is applied directly to the reacting solution via a piston.⁵⁴ Again any reaction containing reagents sensitive to the metal of the block could not be used in this variation. In both types of UV/visible *in situ* monitoring the pressure is applied via a standard array of high pressure pumps and appropriately positioned high pressure rated valves. A direct pressure device is illustrated in Fig. 3.

The advantages are, obviously, a continuous record of the reaction, allowing instant observation of deviations from normal kinetic progress, ability to apply data fitting routines to yield kinetic parameters, and greater results throughput. In reaction systems that require anhydrous or oxygen-free conditions, filling of the pill-box can be carried out in an appropriate glove-box. For oxygen-sensitive reactions a special cell has been developed as well.²² The second method, of applying pressure to a solution directly, has mostly been used for aqueous media and where no restrictions on exposure to air were important. It is worth noting that the piston-cylinder apparatus with aliquot sampling requires typically about 0.1 dm³ of solution per run, the second of the *in situ* methods requires about 0.005 dm³, and the pill-box uses a similar volume of solution as a standard 1 cm path length cuvette (ca. 0.003 dm³). The emphasis has been on UV/visible spectrophotometry since the preponderance of reports in several areas of chemistry exploits this method. A high pressure cell capable of monitoring changes in conductivity has been constructed but not widely used.⁵⁴ In principle circular dichroism, fluorescence or infrared (IR) spectroscopies could also be used as rapid monitoring methods, providing successful interfacing with a high pressure container arrangement is extant. An updated version of a high pressure apparatus, using a pill-box, in which the detection system has been enlarged from UV/visible to the near-IR region and for special circumstances pressures up to 400 MPa may be applied, has been described.⁵⁵

A separate section will be devoted to covering the monitoring of reaction progress at high pressure by nuclear magnetic resonance (NMR) spectroscopy. Although there have been no reports to date, in principle for sufficiently slow reactions aliquot samples from a piston-cylinder apparatus could be followed by NMR spectroscopy; however, such a procedure would not be viable because of the large solution volumes required if deuterated solvents were to be used.

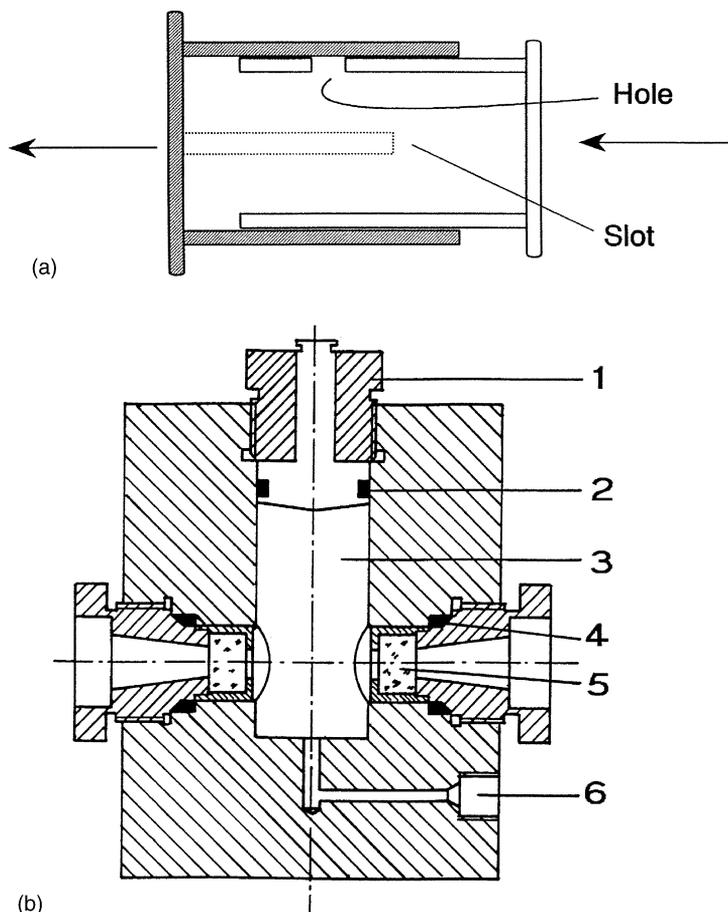


Fig. 2 (a) Schematic presentation of a “pill-box” optical cell for measurements on solutions at high hydrostatic pressures. The slot and hole allow the pill-box cell to be filled and extra liquid to be released on closing the cell. (b) Schematic view of a two-window high pressure cell to accommodate the pill-box optical cell for pressures up to 200 Mpa. 1: pressure plug; 2: O-ring; 3: reaction compartment; 4: Δ - and O-ring; 5: sapphire window and 6: pressure connection.

For situations when temperature or concentration lowering does not achieve the objective of increasing the reaction half-life to a level suitable for the methods described above, a special arrangement for mixing reactants quickly has been devised.²² This device should not be included in the subsequent section on rapid reactions. By mixing quickly here, the term refers to about 5 s, whereas below, mixing times of a few milliseconds are discussed. The reactants are equilibrated thermally and under pressure, but are separated by a thin membrane. The membrane can be broken by a magnetic-field-activated mixing bar, and the mixed solution monitored. Thus the method is suitable for reaction half-lives of about 10 s and longer.

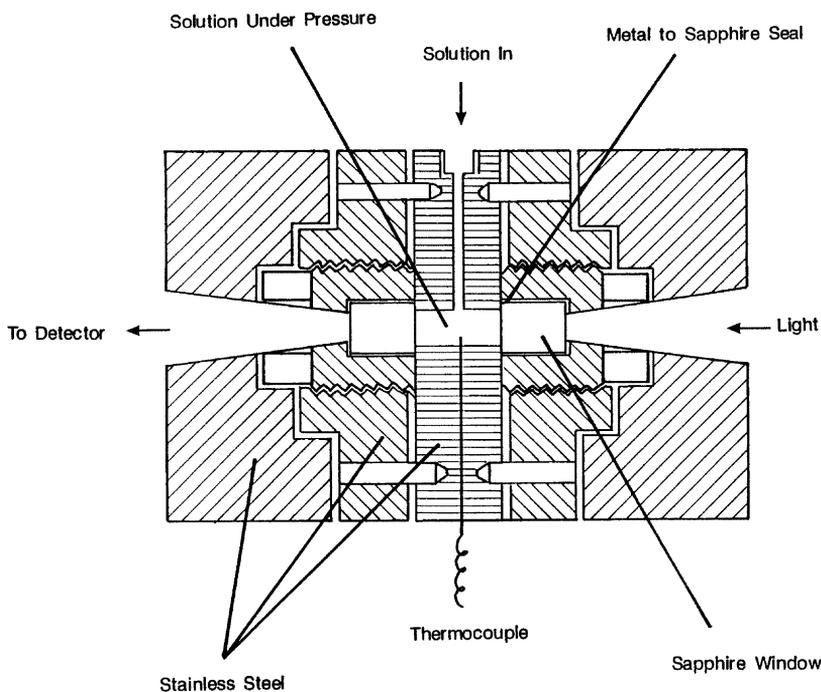


Fig. 3 High pressure cell in which pressure is applied directly to the sample solution.

It should be noted that although high pressure pumps and valves are standard and readily available, most of the high pressure containers and cells have been constructed in individual investigators' laboratories and workshops, and are not commercially available.

RAPID REACTIONS

Mixing methods

This section will be in two parts. First the methods for rapidly mixing reactants at ambient pressure, and subsequently extending this to rapid mixing at elevated pressures, will be described, while a second part will mention methods for studying fast reactions that are complete within the time that the reactant solutions can be physically mixed. Again, adaptation of the latter approach to high pressure will be noted. The methods herein are applicable to thermal reactions. A later section will present methods for reactions that are induced by radiation.

The objective of rapidly mixing reactant solutions for kinetics measurements was first reported about 80 years ago. The method required continuous flowing of solutions, and the term continuous flow was assigned to the method.⁵⁶ Reactant solutions were flowed along tubes and mixed at a Y-type junction. Whereupon

observation and measurement of an appropriate property at given distances from the Y-junction, with knowledge of the flow rate, permitted the development of a kinetic profile. The absence of very rapid detection and rapid flow rates limited the method as large volumes of reactant solutions were needed. Further development took the form of the accelerated-flow method,⁵⁷ and the stopped-flow (s.f.) method. The latter has its origin⁵⁸ in the 1930s and several investigators developed their own version. The history and development of s.f. can be followed.⁵⁹ The reactant solutions are driven manually or by mild pressure activation through a special mixer. The observation chamber is at 90° to the direction of flow in most versions. A rapidly acting receiver syringe with piston that arrests the flow of mixed solution signalled a significant improvement in time resolution.^{60–62} Stopping the mixed solution flow triggers the recording of signal changes. In the usual configurations about 0.15 cm³ of each solution per run is required. Use of an exit valve allows several replicate runs to be conducted before recharging with fresh reactant solutions is required. Commercial versions of s.f. instruments currently available are fundamentally based on some of the early versions, and now, naturally have far superior data collection and processing capability. The instrument dead-time of a few milliseconds means that reactions down to a half-life of several milliseconds can be studied. Almost all instruments use UV/visible signal changes as a means of following kinetics processes. The flow must be turbulent and solution viscosity must be in an appropriate range. The method is not suitable for mixing solutions of widely different ionic strength, or of different solvent composition. Reactions that are markedly exothermic or endothermic can, upon mixing reactants, introduce heating or cooling effects leading to complications that may not be recognised. A rapid mixing device has been coupled to a cell for monitoring reacting organometallic species via IR spectroscopy.⁶³ Other properties of reacting systems, e.g. changes in conductivity, circular dichroism or fluorescence, could also be used in conjunction with the s.f. mixing approach.

Adaptation of the s.f. method to kinetics studies at high pressures (hpsf) can only be viable if the reactant solutions are already under stable thermal and pressure conditions prior to mixing. This has been achieved by immersing an s.f. unit inside a pressurisable container. Another important feature of one design⁶⁴ is that by using smaller quantities of reactant solution than in ambient pressure s.f. units, more measurements can be made before decompression and recharging the unit with fresh reactant solutions are required. This has been accomplished by using the tightness of fit of the stopping and reactant pistons to arrest flow once the applied pressure from a stepping motor to the reactant solution pistons is removed, and there is no outlet valve. In this way about 30 replicate measurements may be made with one filling of the system and allows the system to be compressed to several different pressures before refilling. The windows of the s.f. unit are aligned with windows in the pressurisable vessel, and UV/visible absorbance changes are usually the means of following reaction progress. However, an instrument that monitors fluorescence signals has been constructed and employed.⁶⁵ Several hpsf units have been devised and reported following the first version described by Heremans⁶⁶ and colleagues.^{64,67–74} The technical facts may be consulted. Generally the dead-time is longer than on

ambient pressure s.f. units, although the dead-time has been reduced on some later instruments.^{72,74} Instruments currently in use are either that used in Erlangen or those instruments based on the design of the Merbach group and commercially available,^{69,75} and the other relies on a coupling between the driving and receiving syringes to reduce the dead-time.^{74,76} Figs. 4 and 5 provide schematic illustrations of hpsf instruments.

They have been most widely used to follow the kinetics of ligand substitution and electron transfer reactions of transition metal coordination compounds, although as will be described below also in several organometallic chemistry reaction kinetics studies.

Relaxation methods

When a reaction is faster than the time taken to physically mix solutions other means of following the reaction kinetics must be found. A category of methods, known as relaxation methods, originated in the 1950s.⁷⁷ A reaction system at equilibrium is subject to a rapid perturbation (in principle any property upon which the equilibrium depends can be employed to perturb the equilibrium). The subsequent relaxation to a new equilibrium position is a function of the kinetics of the forward and backward reactions, and the relaxation signal can be analysed to yield kinetic parameters.⁷⁶ Methods of perturbation of equilibrium include a temperature jump, a pressure jump, electric impulse, alternating electrical field, ultrasonic absorption, microwaves and a photochemical flash. The last method will be treated separately in a general section on radiation-induced reactions. Relaxation methods and the methods of analysis of relaxation signals have been included in several publications on fast reactions in solution.^{59,78-83}

Of the relaxation methods only the temperature-jump and pressure-jump methods have been adapted for high pressure application, and of these two only the former (hptj) has been used in many systems for volume of activation determinations. Despite the flurry of activity in developing hptj,⁸⁴⁻⁸⁸ the method has not found application in organometallic chemistry, although in principle it could be employed if the system properties and solvent were suitable.

Details of a standard pressure-jump instrument⁸⁹ and high-pressure pressure-jump cells can be obtained from appropriate literature.⁹⁰⁻⁹³ The method has found very limited application and not at all in organometallic chemistry. Commercial units or modules for high pressure relaxation methods are not available.

RADIATION-INDUCED REACTIONS

Photo-induced methods

In principle reactions that are induced by a light signal could be in the conventional time range, or rapid, requiring rapid data acquisition. The latter class of reactions became a reality in the history of this research area upon the development of fast

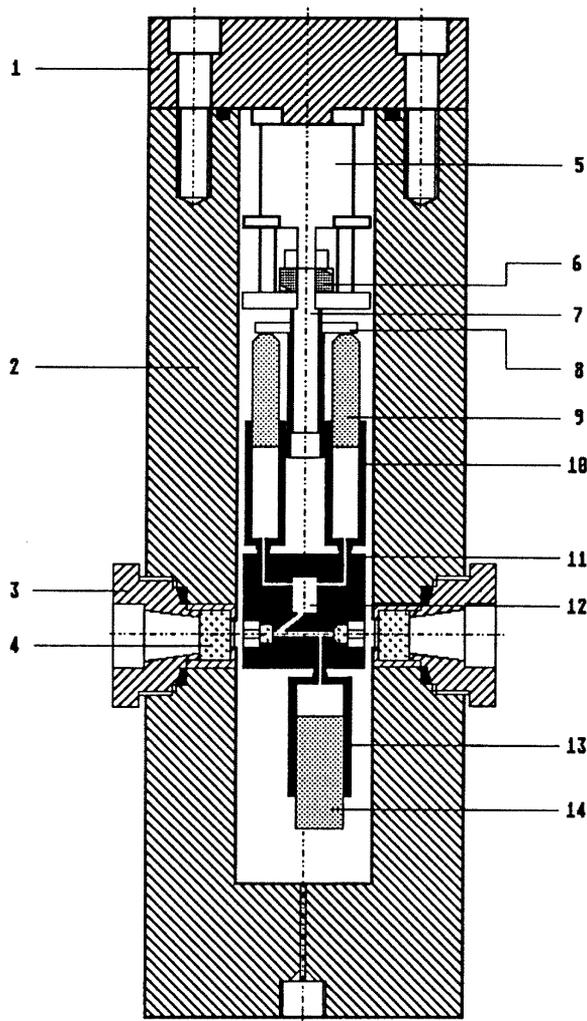


Fig. 4 Schematic presentation of a high pressure s.f. unit. 1: lid to overall unit; 2: outer vessel; 3: window holder; 4: quartz windows; 5: electric motor; 6: motor actuator; 7: s.f. unit positioning rod; 8: syringe driving plate; 9: drive syringe (inner); 10: drive syringe (outer); 11: block holding windows, mixer and syringe attachment points; 12: mixing jet; 13: stop syringe (outer) and 14: stop syringe (inner).

flash lamp technology, and flash photolysis and flash spectroscopy emerged as techniques for studying rapid kinetics of photochemically induced reactions and transient spectra of species in the micro- to millisecond range.⁹⁴ The properties of the system will determine whether the photosensitivity would lead to relaxation kinetics or non-relaxation kinetics. Subsequently the time range of measurement has been reduced by orders of magnitude enabling reactions in the nano- and picosecond

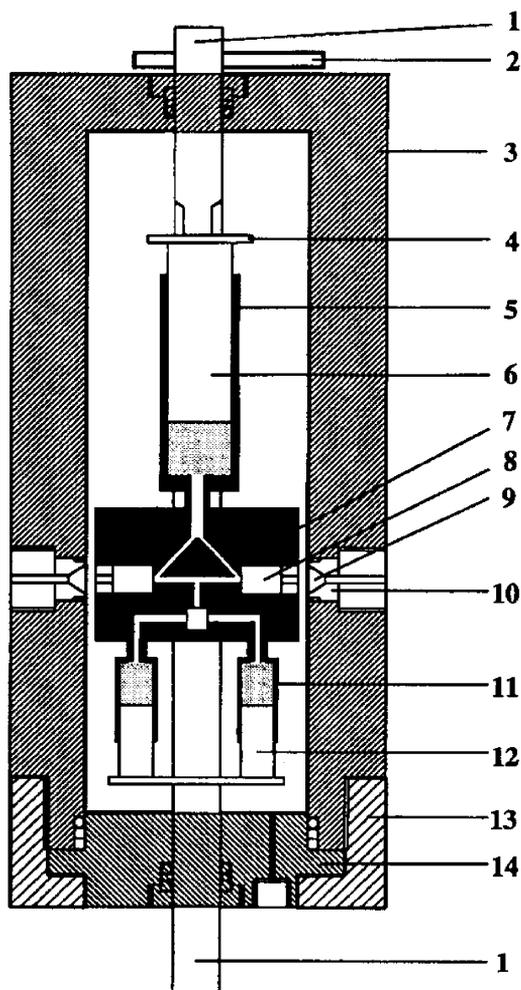


Fig. 5 Cross-sectional diagram of high pressure vessel and s.f. unit. 1: rod made of AISI 316; 2: lever to revolve rod; 3: high pressure vessel; 4: push-pull rod; 5: receiver-syringe piston; 6: receiver-syringe piston; 7: mixer and optical cell block; 8: quartz; 9: sapphire window; 10: sapphire window holder; 11: reactant syringe; 12: reactant-syringe piston; 13: high pressure vessel lid holder and 14: high pressure vessel lid.

range to be studied. Adaptation of these and conventional time methods for high pressure studies of photochemical and photophysical processes was undertaken by several investigators.⁹⁵⁻¹⁰⁰ Examples of some later applications for selected systems are available.¹⁰¹⁻¹⁰⁴ The pill-box cell and enclosing high pressure container can be used, with modification, for slow reactions.¹⁰⁵ In most cases the adaptation involves addition of at least one window in order to be able to initiate reaction and two other windows are used for the subsequent spectrophotometric monitoring of the kinetics.

The high pressure system of pumps and valves need not differ from those used for mixing of reactant solutions. Among organometallic reactions whose kinetics at elevated pressure have been studied following photochemical energy induction are reactions of metal carbonyl complexes. The most frequently used monitoring method is UV/visible spectrophotometry. Time-resolved infrared (TRIR) spectroscopy has been applied recently in studies of iron–carbonyl complexes in supercritical fluids¹⁰⁶ and in studies of molybdenum–carbonyl complexes¹⁰⁷ where moderate gas pressures were used. Although these particular studies did not result in determination of volumes of activation, it is evident that TRIR spectroscopy could be used in appropriate cases in association with high pressure kinetics.

Pulse radiolysis

In this method of inducing reaction, usually in aqueous medium, an electron beam forms radicals from the radiolysis of water in a few microseconds. Subsequent radical reactions with a variety of substrates can be monitored. Authoritative reviews that include results from high pressure kinetics studies have appeared recently.^{108,109} A specially designed pill-box cell has been developed to enable certain radical reactions to be studied at high pressures. An initial difficulty to construct a cell that is sufficiently robust to withstand high pressures, but allows a required level of electron flux to enter the cell, has been overcome by design of a special window (see Fig. 6).¹¹⁰

It should be emphasised that the combination of pulse radiolysis reaction induction and high pressure kinetics capability means that the method is restricted to a very small number of investigators, and commercial units are unavailable. Changes in absorbance in the UV/visible region are used to monitor reaction kinetics. Radical reactions are very rapid and fast data acquisition capability is required. General literature on pulse radiolysis as a method is available.¹¹¹ An account of the value of high pressure kinetics in combination with pulse radiolysis in mechanistic insight provides a survey of the scope and range of reactions studied.¹⁰⁸

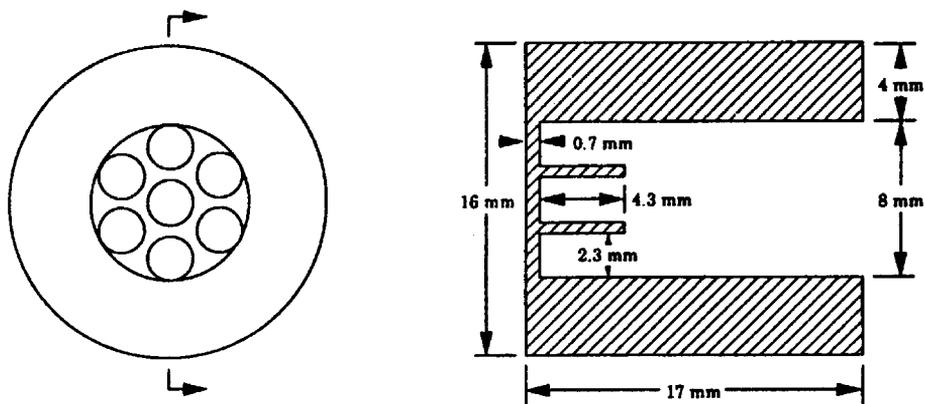


Fig. 6 Schematic diagram of the electron beam window for high pressure pulse radiolysis. The electron beam enters from the right side.

ELECTROCHEMICAL METHODS

The subject of redox reactions embraces a considerable variety of reactions. In homogeneous solution there are many spontaneous reactions, self-exchange reactions or non-symmetrical electron transfer reactions, for example. The kinetics of many of these have been studied by UV/visible spectrophotometry at both ambient and elevated pressures.^{50,112} The kinetic parameters and volumes of activation for some self-exchange reactions have been obtained using ambient and high pressure NMR (HPNMR) spectroscopy, radiochemical tracer methods or s.f. circular dichroism.^{113,114} Some investigators have been interested in redox reactions at electrodes in electrochemical cells. In some cases the purpose was to obtain the volume of activation for a self-exchange reaction indirectly.¹¹⁴ A recent authoritative review has described in detail the methods for studying electrode reaction kinetics, including the more familiar cyclic voltammetry and alternating current polarography methods.¹¹⁵ This review also outlined the relationship between homogeneous versus heterogeneous self-exchange electron transfer, and emphasised the insight obtained from pressure effects. The technology for studying electrode reaction kinetics at high pressure is specialised. A three-electrode cell constructed from Teflon or stainless steel depending on the chemical considerations is sealed inside a thermostatable steel pressure vessel, suitable for pressures up to 400–500 MPa.^{116,117} The design issues and operating difficulties needing to be addressed to ensure successful measurements have been indicated. Of the three electrodes, one is the working electrode, a second is the counter electrode and the third is the reference electrode that is designed to allow ionic contact and to allow compression of the solution in the reference compartment. Overall the cell has a movable piston to allow compression of the reaction medium. As with many high pressure devices, the pressurising fluid is hexane or heptane and is separated from the oil of the hydraulic pump by a piston separator vessel. The pressure dependence of solution viscosity can be significant for organic solvents, but is conveniently negligible for aqueous solutions. How the pressure dependence of solvent viscosity, when applicable, is accounted for has been addressed. Fig. 7 is an example of a high pressure cell and apparatus for electrode kinetics that permits determination of volumes of activation for both coordination and organometallic compound couples.

Other aspects of high pressure electrochemistry kinetics can be obtained from a review by two of the leading experts.¹¹⁸

NMR SPECTROSCOPY

The presence of magnetically active nuclei of sufficient sensitivity and abundance in a reacting system provides a potentially excellent method of monitoring the kinetics of reaction.¹¹⁹ Providing the reaction is sufficiently slow, measurements can commence in a reasonably short time after introduction of the sample into a spectrometer at ambient pressure. One or more signals can be employed in developing a kinetic profile. Adapting NMR probes for measurements at elevated pressures is an exercise that has occupied some investigators from the early period of electromagnet-based

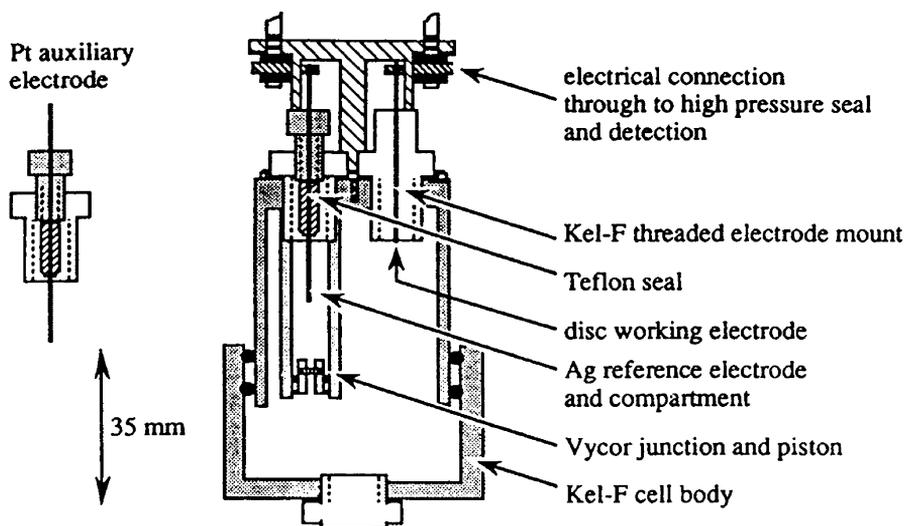


Fig. 7 High pressure electrochemical cell.

spectrometers,^{120,121} to the current generation of high resolution, cryomagnet spectrometers.^{32,122} The development of HPNMR spectroscopy can also be traced from relevant reports and reviews.^{123–125} The adaptation is not simple as materials of the high pressure probe must not interfere with instrument operation. Since an instrument may need to be dedicated to high pressure mode, NMR spectrometers equipped for high pressure measurements are not common laboratory currency.

Pioneering studies by Connick and coworkers led to an understanding of the hydration and lability of the hydration of certain paramagnetic ions.¹²⁶ Using water enriched in ^{17}O , they were able to follow the kinetics of exchange of water between the coordination sphere of each of the aqua ions of Mn(II), Fe(II), Co(II) and Ni(II) and bulk solvent. Kinetic parameters from ^{17}O NMR spectra at various temperatures were extracted from modified Bloch equations. Determination of the water exchange rate constants was important in establishing that rates of complex formation reactions of these metal ions were controlled principally by the respective rates of water exchange. A mechanism embodying these features became known as the Eigen–Wilkins mechanism.^{127,128} Results from hptj experiments on metal-complex-formation reactions yielded positive volumes of activation of magnitudes that supported the mechanism.^{129–132} It also illustrated some time ago the power of high pressure kinetics experiments as strongly confirmative of mechanisms proposed on the basis of ambient pressure kinetics results. Against this background, high pressure probes for NMR (HPNMR) spectrometers that could be used at pressures up to 200 MPa were developed.^{32,122} These instruments have been used extensively to obtain kinetic parameters for exchange of water and other solvents on several transition metal ions, on some main group solvento cations. More recently there has been emphasis on the lanthanides.¹³³ Volumes of activation were also acquired, and also in some cases where non-solvent, non-exchanging ligands are also present. In the context of solvent

exchange on solvento-organometallic compounds, the volume of information is much smaller. Nevertheless, some dramatic effects are observed and will be reported below. Examples of HPNMR probes are shown in Figs. 8 and 9. Details of the construction and materials used are beyond the scope of this article. However, the figures themselves are very illustrative and further details can be obtained.

There has been considerable activity also in developing HPNMR instruments in another and very important area of organometallic chemistry. Conversion of organic substrates into products of greater value, catalysed by organometallic compounds, and understanding the mechanism of individual steps or a whole catalytic cycle, are goals of many investigators. In many reactions the substrate in a solvent is converted and the reaction catalysed in the presence of gases at high pressure. As stated earlier there has been progress in addressing the mechanistic pathways by using HPNMR spectroscopy, using ^{13}C and ^1H nuclei.⁴¹⁻⁴⁴ An objective is to study the reactions as a function of gas pressure to optimise yield as well as elucidate mechanism. Typical pressures are at least an order of magnitude lower than is the homogeneous systems described and volumes of activation are not determined. However, the technical aspects of the instrumentation are of interest and valuable to other high pressure practitioners.

PARTIAL MOLAR VOLUMES FROM DENSITY MEASUREMENTS

Various specification densitometers are available commercially, and operate on the principle of a sound wave whose frequency depends on the density of the solution. The density of air and of the solvent must also be determined. The volume of liquid required is about $2-3\text{ cm}^3$ and each measurement takes only a few minutes. The range of concentrations needed for viable measurements is usually much higher than is used in relevant kinetics experiments and therefore sample solubility, scarcity or solution stability can limit the extent of possible measurement. The need for moderately high concentrations can be seen from examination of Equation (10) since the difference in densities between each solution and the solvent is part of the calculation. In fact densities to six significant figures are usually required. Other critical factors are that the temperature must be precisely ($\pm 0.01\text{ }^\circ\text{C}$, ideally) and reproducibly known since densities are very sensitive to temperature. Highly pure solutes and solvents should be used and solvent outgassing is important. Solute in volatile or mixed solvents do not yield usable results. In addition to obtaining reaction volumes from partial molar volumes of reactants and products, the simple method of dilatometry can be applied.

MISCELLANEOUS TOPICS

Range of values and correlation of ΔV^\ddagger with ΔS^\ddagger

Based on compilations of values of ΔV^\ddagger it can be seen that typical values are within the range of $\pm 30\text{ cm}^3\text{ mol}^{-1}$, although some organic reactions extend that range to

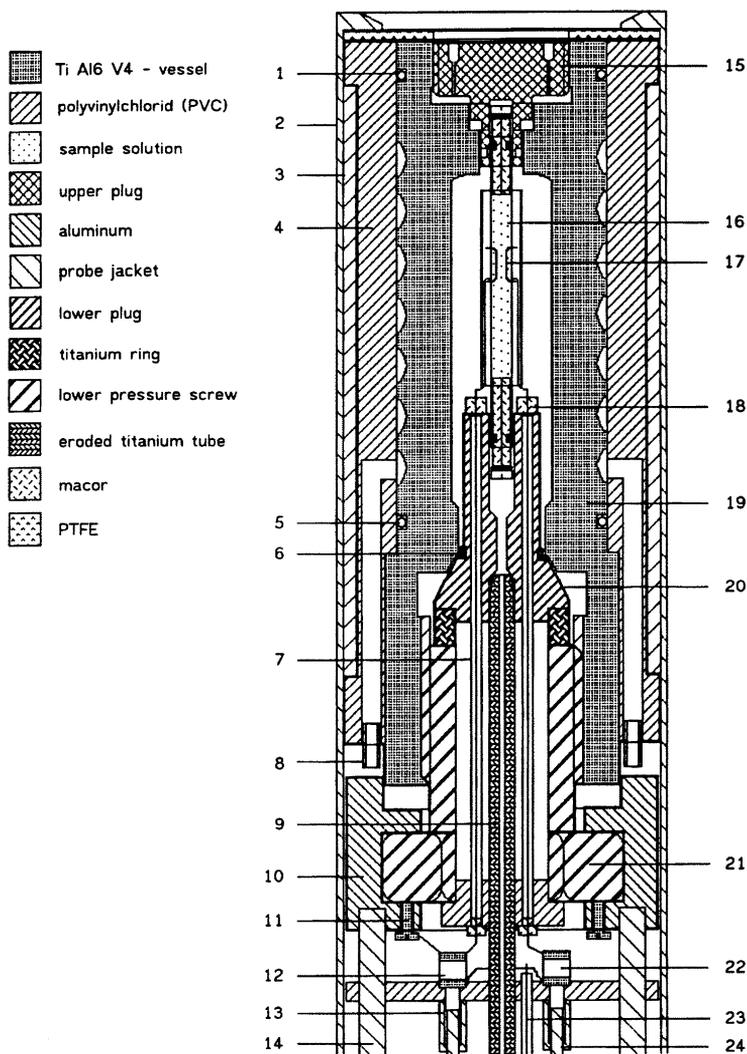


Fig. 8 Design features of a wide bore probe head for HPNMR (400 MHz) measurements. 1: O-ring; 2: probe jacket; 3: thermal insulation; 4: polyvinyl chloride; 5: O-ring; 6: O-ring; 7: semi-rigid coaxial cable; 8: connection to thermostat; 9: titanium tube; 10: lid; 11: screw; 12: capacitor; 13: capacitor holder; 14: aluminium tube; 15: upper plug; 16: sample tube; 17: saddle coil; 18: -Macor; 19: TiAl6V4 vessel; 20: lower plug; 21: lower pressure screw; 22: capacitor; 23: coaxial cable and 24: capacitor holder.

$\pm 50 \text{ cm}^3 \text{ mol}^{-1}$. Volumes of activation of $+30$ or $-30 \text{ cm}^3 \text{ mol}^{-1}$ correspond, respectively, to a rate retardation and a rate acceleration of about a factor of 3.5 at 100 MPa pressure relative to ambient pressure. For these values most methods yield precision of about $\pm 5\%$. For reactions that are less sensitive to pressure the precision is usually progressively reduced as the modulus of the volume of activation is reduced.

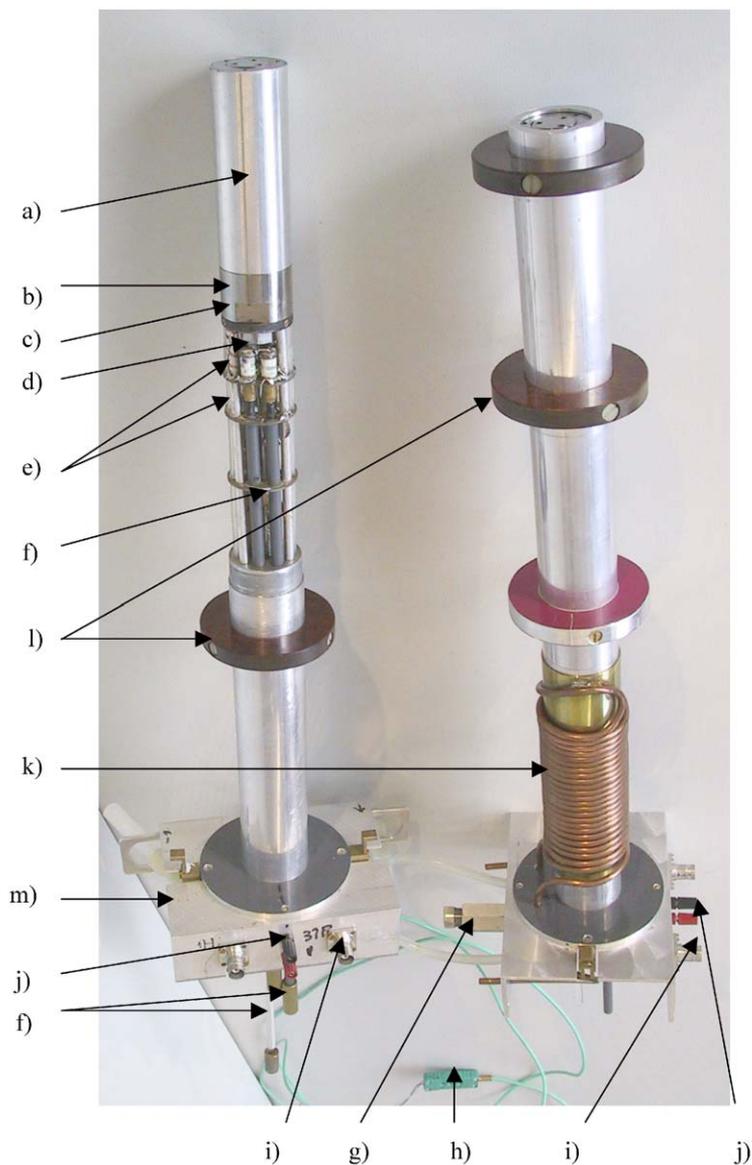


Fig. 9 Photograph of two narrowbore probeheads. a: aluminium jacket sealing the double helix used for thermostating; b: high pressure vessel; c: platform carrying the autoclave; d: capacitors; e: capacitor platforms; f: tuning rods; g: high pressure connector; h: thermocouple; i: BNC connector; j: Pt-100 connector; k: copper tubing and l: widebore adapter.

However, actual precision can depend on the reaction, the particular method of high pressure kinetics measurement and the quality of the instrument. As noted earlier, measurement of pressure at a precision or accuracy of 1–2% is acceptable, as reaction rate sensitivity to pressure would not be detectable within this range.

For many inorganic and bioinorganic reactions the volume of activation has been obtained from measurements at 25 °C. It prevails that the volume of activation is not particularly sensitive to temperature change. This is convenient in that values obtained for different reactions at different temperatures in most cases can be compared directly. Differences at various temperatures for a given reaction can be expected to be within the error of each measurement. Clearly this does not apply to any temperature, and a useful guideline could be that ± 20 °C from the standard 25 °C of measurement should yield no significant difference in the value of ΔV^\ddagger . This can be seen from Equation (9).

When it is experimentally feasible, the temperature dependence of ΔV^\ddagger can be compared with the pressure dependence of the entropy of activation. The equality of these terms is defined from extending the Maxwell thermodynamic equality:

$$(\delta V_i / \delta T)_P = -(\delta S_i / \delta P)_T \quad (11)$$

to an equilibrium or a reaction, viz:

$$(\delta \Delta V / \delta T)_P = -(\delta \Delta S / \delta P)_T \quad (12)$$

$$(\delta \Delta V^\ddagger / \delta T)_P = -(\delta \Delta S^\ddagger / \delta P)_T \quad (13)$$

In some cases the experimental agreement is reasonable.

Several investigators have examined the possible correlation of these two activation parameters, particularly for series of similar reactions.^{134–136} Correlations have been attempted for reactions of transition metal coordination compounds, such as ligand substitution or isomerisation, or solvent exchange,^{135–137} and the issue has been addressed recently.¹³⁸ However, correlations for these parameters for organometallic reactions have not yet been developed.

Safety considerations

Typical sample capacities of solutions in most of the hydrostatic high pressure methods described are in the range of a few cubic centimetres of solution under various compression regimes. A considerably higher volume of the pressurising liquid is maintained at the same pressure. If any component of the overall system under pressure fails liquid leakage can occur and the pressure reverts to ambient immediately. Therefore, the safety aspect is similar to proper laboratory practice in treatment of solvent or solute spillage, particularly if the materials are hazardous or toxic. Since component failure is accompanied by rapid decompression normally, only a fraction of the total liquid that was under pressure will leak. In the case of a piston-cylinder apparatus, the volume of sample can be as high as 0.1 dm³ and therefore the potential for more liquid leakage exists. Providing the pressure is delivered by liquid under pressure, normal safe laboratory practice should be adequate providing the temperature of the system is close to ambient. However, if compressed gases are used to deliver pressure to the pressurisable liquid, then safety practice consistent with other applications of compressed gases is required. When large volumes of liquids, up to 200 dm³, are used in materials processing to bring

about physicochemical change, additional safety measures to protect operators from potentially large volumes of hot liquids leaking must be in place.

3 Volumes of activation for thermal organometallic reactions

In this section a summary of an accepted mechanistic classification scheme will be presented. This scheme applies to many of the organometallic reactions that will be described. Following this, reactions of interest will be grouped together according to their common reaction type, e.g. solvent exchange, ligand substitution, oxidation–reduction, small molecule reactions, photochemically initiated reactions and others. When a particular sub-field of research is currently active, mostly only relatively recent reports will be included and these may be examined for reference to earlier developments in the sub-field. In other cases when a sub-field has become dormant the latest reports generally available will be presented. It should also be emphasised that this account is not an exhaustive one of all volumes of activation determined in recent organometallic chemistry studies. Nevertheless, to our knowledge the vast majority of reports has been included.

A set of generally accepted guidelines for mechanistic diagnosis from volumes of activation has been provided. A mechanistic classification of substitution reactions of transition metal complexes used the letters, D, A and I.¹³⁹ A dissociative process with an identifiable intermediate of lower coordination number is assigned D. An associative process with an identifiable intermediate of higher coordination number is termed an A mechanism. An interchange process, labelled I, is one in which acts of bond breaking and making occur, and either took place within a pre-formed aggregate or were synchronous processes. The I mechanism could be further subclassified into I_d and I_a . The former refers to a dissociatively activated interchange mechanism that has a rate-determining transition state in which bond cleavage is more important than bond formation. Conversely, an I_a mechanism is one that has a transition state in which there is more bond formation than bond cleavage. The nomenclature has been compared with that used for organic reactions.¹⁴⁰ Other often unrecognised subtleties have been considered at length. This literature may be fruitfully consulted.¹⁴⁰ At least for solvent exchange processes, the assignment of mechanism based on ΔV^\ddagger is reasonably straightforward, providing the numerical values are not close to zero, since electrostriction effects are absent or negligible.^{125,141} It has been estimated that for water exchange on an octahedral complex via a D or A mechanism, the value of ΔV^\ddagger would be about $\pm 13 \text{ cm}^3 \text{ mol}^{-1}$, respectively.¹⁴² Values for solvents other than water will clearly differ. If experimental values in water exchange reactions progress from these limits towards zero it has become a practice to assume that these values represent I mechanisms of “d” or “a” character, and that a value of zero would indicate a pure interchange process. The difficulty is that these assignments are based on arguments that take no account of other possible volume changes among the non-exchanging ligands and attendant alterations to the partial molar volume (that are not accessible). It is also noted that for all reactions, volume changes may occur in parts of molecules not involved in the

reaction itself, and these cannot be accounted for or estimated. Nevertheless, as a first approximation the literature contains many mechanistic assignments based on the volume of activation. In the following sections abbreviations used are nearly always those provided by the respective authors.

SOLVENT EXCHANGE

The kinetics and mechanism of solvent exchange from fully solvated or partially solvated metal cations have been extensively studied, mostly by NMR and HPNMR spectroscopies.^{32,133} The range of solvent exchange rates encountered varies over 20 orders of magnitude. The effects of the presence of non-exchanging ligands on both rates and coordination geometry can be very pronounced.^{15,32,133,143–146} Early studies were mostly on the solvento cations or aquamono-hydroxy cations of the first row of transition metals. More recently, reports on solvent exchange kinetics and mechanism of second- or third-row transition metal cations, some main group solvento cations, lanthanide cations and some actinide cations have appeared.^{133,143} The non-exchanging ligands invariably have been coordinating ligands. One reason for these studies, beside their intrinsic interest, is that they assist in understanding metal-complex-formation reactions in which one or more solvent molecules is/are replaced by a coordinating or chelating ligand. In the case of some lanthanide ions the development of appropriately functioning magnetic imaging reagents for medicinal purposes, composed of solvento complexes of lanthanides, drives the studies forward. Theoretical studies conducted on several of these solvent exchange reactions have usually shown accord with the mechanisms based on experimental activation parameters including the volume of activation.^{147–153}

Dramatic changes in the kinetic lability of solvent exchange have been observed when some of the coordinated solvent molecules are replaced by an organic moiety. For example, hexa-aqua ruthenium(II) has a water exchange rate constant of $1.8 \times 10^{-2} \text{ s}^{-1}$ at 298 K,¹⁵⁴ while water exchange on $\text{Ru}(\eta^5\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_3^{2+}$ is characterised by a rate constant of 11.5 s^{-1} at the same temperature.¹⁵⁵ Clearly the water exchange mechanism for the arene-aqua ions is characterised by a strong *trans*-labilising effect of the aromatic ligand on coordinated water. The thermal activation parameters, ΔH^\ddagger of 88 and 76 kJ mol^{-1} and ΔS^\ddagger values of +16 and +30 $\text{J mol}^{-1} \text{ K}^{-1}$ for the hexa-aqua and aqua-arene complexes, respectively, would imply that the change in free energy of activation is a consequence of both parameters. However, the magnitude of error on the entropy of activation values is such that the two values are not statistically different. The volumes of activation, -0.4 and $+1.5 \text{ cm}^3 \text{ mol}^{-1}$ for the hexa-aqua and the arene-aqua complex, respectively, indicate an interchange mechanism with approximately equal contributions of bond breaking and bond making for the former species. The latter value indicates an interchange mechanism in which bond breaking is slightly ahead of bond making, according to the authors. However, these findings can hardly be definitive given the small difference and errors associated with both values. Interestingly the osmium(II) analogue, $\text{Os}(\eta^5\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_3^{2+}$, has the same solvent exchange rate constant as the corresponding ruthenium

compound,¹⁵⁵ and is characterised by a 10 kJ mol^{-1} smaller enthalpy of activation, an essentially zero entropy of activation and a modest, $+2.9 \text{ cm}^3 \text{ mol}^{-1}$, volume of activation. The latter parameter suggests a slightly more dissociative interchange mechanism than for the ruthenium water exchange. The lack of proof for the existence of a hexa-aqua osmium(II) species, has been noted^{156,157} and therefore a comparison that could be made in the ruthenium case cannot be made for the activation parameters for the osmium species.

Even more dramatic rate enhancements occur for acetonitrile exchange on solvento-, arene-solvento- and cyclopentadienyl-solvento-ruthenium(II) complex species. The substitution lability of CH_3CN increases along the series $\text{Ru}(\text{CH}_3\text{CN})_6^{2+}$, $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{CH}_3\text{CN})_3^+$, $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_3\text{CN})_3^+$ by five orders of magnitude for each step. The kinetics were monitored by ^1H NMR spectroscopy.¹⁵⁸ The increase correlates with a corresponding stepwise lengthening of the Ru–N distance by 0.03 \AA , and indicates the significant progressive *trans*-labilisation enhancement. Enthalpy of activation decrements were, respectively, 28 and 16 kJ mol^{-1} . The values of ΔV^\ddagger provide clear evidence for mechanistic change. For the solvento cation the value was $+0.4 \text{ cm}^3 \text{ mol}^{-1}$, whereas the values were $+2.4$ and $+11.1 \text{ cm}^3 \text{ mol}^{-1}$ for the arene and cyclopentadienyl species respectively, interpreted as interchange, interchange dissociative and dissociative, respectively. From the findings for both solvents it may be speculated that $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{H}_2\text{O})_3^+$ should exchange water ligands very rapidly.

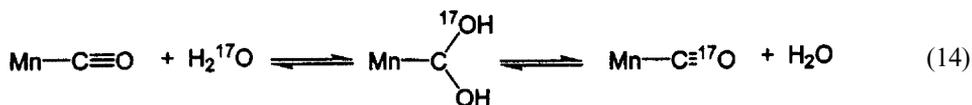
A comprehensive preparative, structural and kinetics study (of water exchange and substitution) of several π -arene complexes of cobalt, rhodium, iridium and ruthenium has been undertaken.¹⁵⁹ As noted earlier, π -arene molecules upon substituting water molecules in $[\text{M}(\text{H}_2\text{O})_6]$ (charges omitted) to yield $[\text{LM}(\text{H}_2\text{O})_3]$, $\text{L} = \eta^6\text{-benzene}$ or $\eta^5\text{-pentamethylcyclopentadienyl}$ ion (Cp^*), $\text{M} = \text{Co, Rh, Ir, Ru}$, increase the lability of the three residual water molecules drastically. The effect is most pronounced for anionic ligands. The labilisation effect is neutralised by two orders of magnitude when two of the surviving water molecules are replaced by 2,2'-bipyridine (bpy). There is a strong effect of the variation of metal ion with the lability of coordinated water in $[\text{Cp}^*\text{M}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ following the order $\text{Co} \ll \text{Rh} < \text{Ir}$. Thermal activation parameters and a series of kinetics results on formation reactions by s.f. spectrophotometry provided evidence that could be interpreted to show that water exchange on $[\text{Cp}^*\text{M}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ proceeds by a dissociative interchange mechanism. The rates of water exchange in $[\text{Cp}^*\text{M}(\text{H}_2\text{O})_3]^{2+}$ ($\text{M} = \text{Rh, Ir}$) were followed at ambient and elevated pressures, by ^{17}O NMR spectroscopy, yielding respectively activation volumes of $+0.6$ and $+2.4 \text{ cm}^3 \text{ mol}^{-1}$. These values are indicative of an interchange mode of mechanism with a modest dissociative character.

Attention has been drawn to the connection between mechanisms of solvent exchange for arene–osmium compounds cited earlier and on dihydrogen–amine complexes of osmium, *trans*- $[\text{Os}(\text{en})_2(\eta^2\text{-H}_2\text{S})]^{2+}$, $\text{S} = \text{H}_2\text{O, CH}_3\text{CN}$.¹⁶⁰ The values of the volumes of activation for solvent exchange from ^{17}O NMR (H_2O exchange) or ^1H NMR (CH_3CN) spectroscopy were -1.5 and $-0.5 \text{ cm}^3 \text{ mol}^{-1}$, respectively. At face value parameters of this magnitude would be indicative of an I mechanism. However, it was argued from results of complex-formation reactions, and a previously cited argument, that the volumes of activation were also influenced by a contraction

of bonds of the metal to the non-reactive ligands. Thus solvent exchange on these osmium–dihydrogen complexes was dissociative interchange, I_d or dissociative, D . Therefore, it is a similar mechanistic situation to the I_d mechanism for water exchange on the osmium organometallic complexes.

It has been pointed out that ruthenium(II) possesses properties that allow it to be a focus of studies of organometallic chemistry of Ru(II) in water.¹⁶¹ In addition some Ru(II) aqua complexes are key intermediates in processes connected with anti-tumour activity of Ru(II) and Ru(III) compounds.¹⁶² These facts formed part of the interest behind studies aimed at understanding factors that govern the reactivity of ligands in the first coordination sphere of the Ru(II) centre.¹⁶³ Specifically the effect of L (L = H₂O, CH₃CN, (CH₃)₂SO, H₂C = CH₂, CO, F₂C = CH₂, N₂) on the rates of bound water at the axial (*trans*) and equatorial (*cis*) positions and on the redox potentials of [Ru(H₂O)₅L]²⁺ has been examined. Compared with square planar complexes *cis* and *trans* effects on reactivities are less well understood in complexes of octahedral geometry. The kinetics of water exchange were monitored by ¹⁷O NMR spectroscopy, and in the case of the ethene compound as a function of pressure. The kinetics results set the order of L for both *cis* and *trans* effects, and a correlation between lability and calculated Ru–H₂O_{ax} bond energies was indicated. Density functional theory was used to calculate properties of the ruthenium species. Rate constants for mono-complex formation between the ruthenium aqua ion and different ligands were very similar and an interchange I_d mechanism was assigned even though ΔV^\ddagger for water exchange on hexa-aqua Ru(II) was close to zero (vide supra). The ΔV^\ddagger values for water exchange on the axial and equatorial positions of the ethene complexes are +6.5 and +6.1 cm³ mol⁻¹, respectively, and reflect the strong dissociative character of the mechanism. Large positive values of the entropy of activation supported this conclusion.

It was recognised that most of the earlier work on solvent exchange on organometallic–solvent–complexes featured second- (4d) or third-row (5d) transition metals. An extension to the first row was sought for the Group VII carbonyl aqua ions [(CO)₃M(H₂O)₃]⁺, M = Tc, Re.¹⁶⁴ There was a degree of uncertainty about the authenticity of the species when M = Mn, but a spectroscopic characterisation has confirmed the species as *fac*-[(CO)₃Mn(H₂O)₃]⁺.¹⁶⁴ The aqueous solution characteristics of this species strongly depend on the solution pH and the formation of polynuclear metal species is prevalent but not identical for the rhenium and manganese analogues. Species interconversion rates are also different. The 1+ oxidation state for these species is considered to arise from CO groups stabilising the t_{2g} orbitals by back bonding, effecting a low-spin configuration and by shifting the oxidation potential M^{2+/+} to a more positive value, thus stabilising the monovalent species. Under appropriate solution conditions, the water exchange process on [(CO)₃Mn(H₂O)₃]⁺ can be monitored by ¹⁷O NMR spectroscopy. The interpretation of signal intensity changes indicated that carbonyl oxygen exchange occurs as shown below:



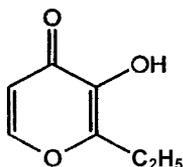
This type of exchange was not observed for the corresponding rhenium compound. Fitting procedures from studying the water exchange rate at different temperatures yielded k_{ex} at 298 K of 19 s^{-1} , and $\Delta H^\ddagger = 68\text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 8\text{ J mol}^{-1}\text{ K}^{-1}$. The exchange rate constant shows that water exchanges almost four orders of magnitude faster than on the corresponding rhenium compound. A preliminary value for water exchange on the Tc compound is sufficient to show that the exchange rate decreases in the order $\text{Mn} > \text{Tc} > \text{Re}$. This was suggested to be consistent with the order of water exchange on $\text{Co}^{3+}/\text{Rh}^{3+}/\text{Ir}^{3+}$ aqua ions. However, the strong labilising effect of Cp^* , more prominent for the heavier metals, reverses this lability order of water exchange on $[\text{Cp}^*\text{M}(\text{bpy})(\text{H}_2\text{O})]^{2+}$, $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$.¹⁵⁹ The activation volume for water exchange on $[(\text{CO})_3\text{Mn}(\text{H}_2\text{O})_3]^+$ is $-4.5\text{ cm}^3\text{ mol}^{-1}$, indicative of an associative activation mode (I_a or A). On the basis of a volume of activation determination the water exchange mechanism on the rhenium cation is interpreted as I_d , a contrasting finding, and an unexpected trend. At present the substitution of water by another ligand on $[(\text{CO})_3\text{Mn}(\text{H}_2\text{O})_3]^+$ has yet to be investigated and therefore cannot be compared with the situation pertaining to the rhenium analogue, where the substitution mechanism appears to undergo a changeover from I_d with a hard donor, to I_a for a soft donor.¹⁶⁵

LIGAND SUBSTITUTION

In this section the coverage follows mainly in order of the atomic number of the pertinent metal. However, in some cases when corresponding reactions of two metal centres (MCs) have been investigated the sub-section relates to both MCs.

Titanium

Titanium(IV) compounds of the general type $\text{Ti}(\text{LL})_2\text{X}_2$, where LL is a bidentate anionic ligand and X is a halide or alkoxide, have been shown to possess anti-tumour activity.¹⁶⁶ The cyclopentadienyl compound $\text{Ti}(\text{Cp})_2\text{Cl}_2$ has been studied and some kinetic characteristics established.¹⁶⁷ It is considered possible that the pharmacological activity resides in the Cp group, but other LL groups, e.g. the benzoylacetato moiety in $\text{Ti}(\text{bzac})_2(\text{OEt})_2$, confers activity on this compound,¹⁶⁸ although there are some disadvantages in its application.¹⁶⁹ A search for other efficacious compounds focused on pyrones (see Scheme 1) and pyridinones, since anions of these ligands formed stable titanium(IV) complexes $\text{Ti}(\text{LL})_2\text{X}_2$. (Pyrones with $\text{R} = \text{Me}, \text{Et}, \text{maltol}$ and ethylmaltol are permitted as food additives.)



Scheme 1.

Solvolysis and substitution rates are known to be important for platinum anti-tumour agents,¹⁷⁰ and consequently these properties of titanium(IV) complexes containing pyronato and pyridinato ligands and halide or alkoxide leaving groups were examined.¹⁷¹ Earlier studies on the kinetics of substitution at $\text{Ti}(\text{Cp})_2\text{Cl}_2$ ¹⁷² were extended to include the influence of hydrostatic pressure.¹⁷¹ A wide-ranging kinetics study examined the effects of the non-leaving ligand, the leaving ligand and various entering (substituting) ligands on the rates for substitution at $\text{Ti}(\text{LL})_2\text{X}_2$, where LLH = cyclopentadiene, the 4-pyrone ethylmaltol, several 4-pyridinones and related ligands with X = halide or alkoxide in acetonitrile, spectrophotometrically. Two reaction stages were observed and of sufficiently different rates that rate constants (first order for each, entering ligand in excess concentration) could be obtained. Analysis indicated a two-term rate law for each step consisting of a solvolysis pathway and a bimolecular attack. The stages refer to the successive removal of the departing ligands. The substitution reactions of NCS^- with $\text{Ti}(\text{Cp})_2\text{Cl}_2$ and of H_2O with $\text{Ti}(\text{Etmalt})_2\text{Cl}_2$ for the second stage were studied at pressures up to 100 MPa and derived activation volumes for bimolecular attack were -15 and $-12 \text{ cm}^3 \text{ mol}^{-1}$, respectively. These values are of the magnitude expected for a bimolecular process in the absence of solvent effects.¹¹ Hydration effects have a significant impact on activation volumes for bimolecular inorganic reactions involving small hydrophilic anions such as hydroxide or cyanide in aqueous solution.^{173,174} These effects can be attributed to extensive desolvation of the anionic nucleophile as it enters the transition state. In acetonitrile the situation will be very different since dipolar aprotic solvents solvate hydrophilic anions poorly. The transfer chemical potential of thiocyanate from water into acetonitrile of $+12 \text{ kJ mol}^{-1}$ or greater indicates that thiocyanate is essentially unsolvated in acetonitrile.¹⁷⁵ Therefore, in this situation a solvation contribution to the activation volumes for thiocyanate attack at these Ti(IV) species can be thought to be negligible, so that the negative values afford strong support for a bimolecular associative mechanism for that pathway.

Vanadium

In a partly parallel study to that reported for titanium(IV) above, the kinetics of substitution at vanadium(IV) in bis-cyclopentadienyvanadium dichloride by a range of anionic and uncharged nucleophiles (L) in acetonitrile have been investigated.¹⁷⁶ Such compounds were originally prepared over 50 years ago,¹⁷⁷ and some aspects of the kinetics of substitution have subsequently been studied.¹⁶⁷ As in the corresponding report on titanium(IV) compounds, by employing a wider range of incoming nucleophile concentrations, substitution of both chloro groups from $\text{V}(\text{Cp})_2\text{Cl}_2$ could be observed, spectrophotometrically, and characterised. In an earlier report only one stage was detected.¹⁷² Moreover, the two steps were sufficiently different in rate that rate constants could usually be determined accurately. Each of the two steps followed a two-term rate law, and in the first step the nucleophile concentration-independent rate constants are essentially identical as expected for a rate limiting solvolysis. For the second stage there is some variation in the solvolysis term, a finding to be expected since the substrate has progressed from $\text{V}(\text{Cp})_2\text{Cl}_2$ to

$V(Cp)_2ClL$, where L has displaced Cl in the first stage. The rate constants for the nucleophile concentration-dependent part of the rate law for the first stage showed variation as expected for associative attack, and generally the variations were qualitatively consistent with expectations of relative nucleophilicity of the entering groups, and with a similar pattern as found for reactions of $Ti(Cp)_2Cl_2$. Both entering ligand and V(IV) species differ for the nucleophilic attack in the second stage. Therefore, it would be difficult to comment on the relative values of the second-order rate constants. High pressure kinetics measurements for the reaction of $V(Cp)_2Cl(NCS)$ with NCS^- yielded a value of $-12\text{ cm}^3\text{ mol}^{-1}$, supporting the associative nature of the reaction, and comparable to the value of $-15\text{ cm}^3\text{ mol}^{-1}$ for the corresponding reaction at Ti(IV). Reactions were slower at vanadium, and this was accounted for from Crystal Field considerations, d^1 (V) versus d^0 (Ti) ions.

Manganese

The reporting of a rhenium *fac*-tricarbonyl species containing two β -alanine ligands, functioning as unidentate ligands, and a bromo ligand, formed by reacting rhenium pentacarbonyl bromide with β -alanine,¹⁷⁸ was followed by a study of the analogous reaction between manganese pentacarbonyl bromide and β -alanine.¹⁷⁹ In the latter case the kinetics of the reaction in different solvents were studied and some activation parameters acquired. For the reaction in both 50% aqueous methanol and 50% aqueous dimethyl sulphoxide, two kinetically distinct steps were observed, the first-stage proceeding in the dark and the second-stage proceeding only in light. The entering β -alanine ligand, and in parallel experiments using glycine as the entering ligand, the amino acid was in excess over the concentration of the manganese species, in which case the kinetics were first order, and were monitored spectrophotometrically. In all cases, except for the first stage of the reaction of $Mn(CO)_5Br$ with β -alanine in 50% aqueous dimethyl sulphoxide, all first-order rate constants were independent of the concentration of entering amino acid concentration. A two-term rate law containing a solvolysis (dissociative) term and an associative pathway was indicated from the analysis of results for the first stage of the reaction of β -alanine with $Mn(CO)_5Br$ in 50% aqueous dimethyl sulphoxide. All other reaction steps were regarded as following a dissociative mechanism, although the difference of a factor of three for the rate constant (first stage) for reaction of β -alanine compared with glycine demonstrated that the dissociative mechanism was not entirely straightforward. For the second stage, first-order rate constants were independent of the concentrations of $Mn(CO)_5Br$, β -alanine or glycine, and independent of solvent suggesting a dissociative reaction mechanism. The difference in mechanisms for the first reaction stage was attributed to the markedly higher chemical potential of β -alanine in 50% aqueous dimethylsulphoxide. Activation parameters for reaction of $Mn(CO)_5Br + \beta$ -alanine (first stage) were 121 kJ mol^{-1} , $+84\text{ J mol}^{-1}\text{ K}^{-1}$ and $-20\text{ cm}^3\text{ mol}^{-1}$ for ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger , respectively. It was difficult to reconcile each of these values with a simple dissociative mechanism. A positive volume of activation would be expected for a dissociative mechanism. It was suggested that the amino acids (acting with different rates as referred to above) have specific but

different interactions with the manganese species. Drastic solvent reorganisation about the amino acid occurred as it went from a zwitterionic form in solution to a non-zwitterionic form in the pentacarbonyl manganese derivative. It was also proposed that the $\text{Mn}(\text{CO})_5\text{Br}$ -amino acid interaction is complete over the whole range of amino acid concentrations covered, but that the strength of the interaction depends on the nature of the amino acid involved. It was also pointed out that the entropy and volume of activation were not compatible with a correlation that might be expected.¹⁸⁰ Hence, although rationalisations for these results were provided, the magnitude and sign of the volume of activation remained puzzling.

A subsequent study¹⁸¹ in which the kinetics of substitution of two CO molecules by bidentate ligands in $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) were monitored yielded distinctly positive volumes of activation. The ligands were dab (biacetyl bis(phenylimine) a diazabutadiene), dabCl (biacetyl bis(4-chlorophenylimine), dab- OCH_3 (biacetyl bis(4-methoxyphenylimine), phen (= 1,10-phenanthroline) and bpy. Toluene or dichloroethane were the solvents employed, solvents that are markedly less polar than those in the previously cited study. The rate constant for product ($\text{Mn}(\text{CO})_3(\text{LL})\text{X}$) formation was independent of the incoming ligand. In toluene the thermally derived activation parameters were very similar for the reactions of $\text{Mn}(\text{CO})_5\text{Cl}$ and the bromo analogue with dab and for the reaction of the chloro compound with dab- OCH_3 . For reaction of $\text{Mn}(\text{CO})_5\text{Cl}$ with dab, a volume of activation of $+20.6 \text{ cm}^3 \text{ mol}^{-1}$ was obtained. All of these findings pointed towards a limiting D mechanism in which the rate constant represents the rate of dissociation of a *cis*-CO ligand from $\text{Mn}(\text{CO})_5\text{X}$ to form a five-coordinate species. The product species $\text{Mn}(\text{CO})_3(\text{dab})\text{Cl}$ was confirmed to be a distorted octahedron with a facial arrangement of the three CO groups. It was also noted that the absence of a solvation contribution (no charge or significant polarity changes in the rate-determining step, and a non-polar solvent) means that the experimental volume of activation is virtually identical with $\Delta V_{\text{intr}}^\ddagger$. The chloro compound reacted about 10 times faster than the bromo compound, a fact related to the stronger electronegativity of the chloro ligand that reduced the electron density on Mn. Hence the extent of bond-stabilising π -back bonding to CO was also reduced. As could be predicted for a reaction not involving highly polar species, there was only a very modest decrease in rate when the reaction was conducted in the more polar dichloroethane.

Iron and molybdenum

The second-order term in the rate laws for reactions of low-spin iron(II)-diimine complexes with such nucleophiles as hydroxide and cyanide ions has been established as arising from a bimolecular reaction between complex and nucleophile.¹⁸² Activation volumes that were obtained for reactions of CN^- and OH^- with $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Fe}(\text{bpy})_3^{2+}$ were in the range of $+19.7$ to $+21.5 \text{ cm}^3 \text{ mol}^{-1}$.¹⁸³ Because these observations were not readily accounted for by an associative mechanism, a mechanism analogous to the Eigen–Wilkins mechanism of complex formation was introduced in which dissociative activation dominates in determining the observed activation volumes. However, subsequently it was shown that solvation

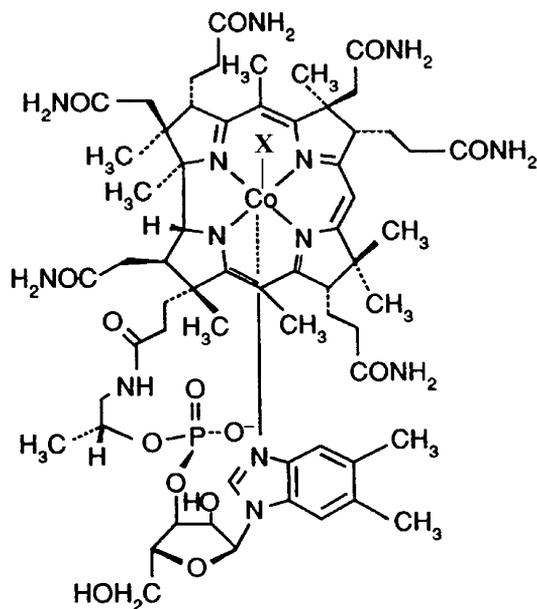
effects, specifically desolvation of the anionic nucleophile could play a large part in determining the sign and magnitude of the volume of activation in this type of reaction.⁴⁹ The approach that led to this proposal involved studying the kinetics of substitution reactions of iron(II)-tris-diimine complexes and of molybdenum–diimine–tetracarbonyl complexes, in various solvents, at elevated pressures and made use of transfer chemical potential data of the relevant entering nucleophile (the cyanide ion).⁴⁹ In dimethylsulphoxide and methanol, respectively, the volumes of activation for reaction of cyanide with $\text{Mo}(\text{bpy})(\text{CO})_4$ were -9 and $+4 \text{ cm}^3 \text{ mol}^{-1}$. The same bimolecular mechanism would be expected for reaction of CN^- with $\text{Fe}(\text{4-Me-phen})_3^{2+}$, yet for the reactions in a methanol water mixture and aqueous solution were $+13$ and $+10 \text{ cm}^3 \text{ mol}^{-1}$, respectively. Gibbs free energy of transfer of the cyanide ion from water into mixed and non-aqueous media suggest markedly lower solvation of the cyanide ion in methanol than in water and less solvation still in dimethyl sulphoxide. Thus the value of the volume of activation for reaction of cyanide with $\text{Mo}(\text{bpy})(\text{CO})_4$ is consistent with expectation for a bimolecular associative mechanism, and a small or negligible contribution in a positive direction from cyanide desolvation. The increasingly less negative to positive values of the volume of activation reflected qualitatively the increasing contributions to it of cyanide ion desolvation. Clearly other factors can assume some importance as there are differences in the value of ΔV^\ddagger for cyanide and hydroxide attack at similar iron (II)–diimine complexes. This issue has been addressed in later reports.^{45,48} However, this early report highlights application of a combination of the volume of activation parameter and other thermodynamic quantities (transfer chemical potentials, $\delta_m \mu^\ominus$) in a successful attempt to resolve mechanistic issues.⁴⁹

Further employment of a combination of equilibrium and high-pressure-derived kinetic parameters enabled insight to be provided into the mechanism of cycloaddition of tetracyanoethene to tricarbonylcycloheptatrieneiron.⁵¹ This reaction initially was reported to yield a 1,5-adduct,¹⁸⁴ but this was later shown to arise from isomerisation of a 1,3-adduct.¹⁸⁵ Interest in determining whether this cycloaddition reaction proceeds via a concerted or a stepwise dipolar mechanism has stimulated frontier orbital calculation predictions.¹⁸⁶ The finding of a lack of a significant solvent effect was significant¹⁸⁷ and the high dienophile dependence of the rate of addition was noted.¹⁸⁸ These studies pointed towards the concerted mechanism. In order to obtain direct information on the nature of the transition state, a study to determine the activation volumes in solvents of widely differing polarities, and to examine the effects of the same solvents on the initial and final states was undertaken.⁵¹ The reaction had been established previously to be second order (first order in each reactant) in dichloromethane and acetone- d_6 at ambient pressure,^{187,189} and the same rate law pertained for the reaction in acetonitrile. The volume of activation obtained from kinetics measurements by monitoring the reaction spectrophotometrically was statistically the same ($-31 \text{ cm}^3 \text{ mol}^{-1}$) in dichloromethane, acetone and acetonitrile. A highly ordered transition state could be inferred from the magnitudes of the entropy of activation (-165 to $-145 \text{ J mol}^{-1} \text{ K}^{-1}$), similar to the values encountered in Diels–Alder reactions,¹⁹⁰ and indicated concerted bond formation. Closely similar values of the enthalpy of activation were obtained for the reaction in

each solvent. This would not be expected for a pathway involving a zwitterionic intermediate, since such a pathway would exhibit a spread of enthalpies of activation reflecting the changes in transition state solvation in the different solvents. From solubility measurements on both reactants and the product, transfer chemical potentials for transfer from the low polarity dichloromethane to acetone and acetonitrile could be calculated. Changes in the Gibbs energy of activation, calculated from the rate constants then permitted calculation of the transfer chemical potential for the transition state. The values of the transfer chemical potential for acetone and acetonitrile were intermediate between those for the initial state and the final state demonstrating that there is no increased solvation of the transition state that would have been anticipated for a dipolar transition state in polar solvents. Taken together, an analysis of the activation parameters and the transfer chemical potentials clearly provided support for a concerted mechanism.

Cobalt

There is substantial literature on cobalt-containing compounds in which a carbon–cobalt bond is in an axial position *trans* to usually an N-donor ligand, with the four equatorial positions occupied by N-donors too. This coordination arrangement is present in adenosylcobalamin (AdoCbl, coenzyme B₁₂) and in cyanocobalamin (CNCbl, vitamin B₁₂). The *trans* N-donor is dimethylbenzimidazole (DMBz) attached to a nucleotide (Scheme 2).



Scheme 2 Structure of cobalamin, where X = CN⁻ for cyanocobalamin (vitamin B₁₂), X = H₂O for aquacobalamin (vitamin B_{12a}) and X = 5'-deoxyadenosyl for coenzyme B₁₂.

Interest has been further stimulated by accounts of variable manipulation of axial ligation by different enzymes. Naturally the establishment of relevant kinetic and thermodynamic properties of processes that control cleavage of the cobalt-carbon bond and understanding the influence of the ligand *trans* to the bond are priorities, as well as is the development of correlations of such properties to structural characteristics. Investigations have taken several forms using the cited compounds themselves and analogues and model species. For example, a very recent investigation made use of a compound in which the DMBz moiety has been replaced by the less bulky imidazole in the compound cyanoimidazolcobamide (CN(Im)Cbl).¹⁹¹ One focus of some recent investigations is characterising the base-on/base-off equilibrium in which the axially coordinated DMBz- or Im-nucleotide is displaced by water and protonated.¹⁹² In addition, the kinetics of axial ligand substitution in the case of vitamin B₁₂ derivatives and model complexes have been examined in detail. These studies have benefitted in terms of mechanistic insight from application of high pressure techniques. An earlier lack of clarity in overall mechanistic understanding is being replaced by a more coherent understanding.¹⁹³ Mostly reports from the past few years will be highlighted.

The kinetics of substitution of coordinated water or methanol by three pyridine nucleophiles (pyridine itself and the 4-CN- and 4-NH₂-derivatives) in *trans*-RCo(Hdmg)₂(H₂O) or *trans*-RCo(Hdmg)₂(CH₃OH) (R = C₆H₅CH₂ or CF₃CH₂ and dmg = dimethylglyoxime), have been studied as a function of nucleophile concentration, temperature and pressure.¹⁹⁴ An analysis of the derived activation parameters led to the conclusion that the substitution mechanism varies with the R-substituent and solvent. Thus a limiting D mechanism was proposed when R = C₆H₅CH₂, reflecting a stronger donor property than when the substituent is CF₃CH₂ for which case an I_d mechanism was indicated for water substitution. The mechanism also varies in that the trend in ΔV^\ddagger values depended on the basicity of the nucleophile with progressively increasing positive ΔV^\ddagger values (4-CN- > H- > 4-NH₂-). An extension to this study used a wide range of different entering nucleophiles to displace the axial ligand in *trans*-[Co(Hdmg)₂(R)S] with R = Me and PhCH₂ and S = H₂O or CH₃OH, in order to determine the role of the nucleophilicity of the entering ligand and the nature of R on the reactivity of the Co(III) centre.¹⁹⁵ The entering ligands were imidazole, pyrazole, 1,2,4-triazole, *N*-acetylimidazole, 5-chloro-1-methylimidazole, NO₂⁻, Ph₃P, Ph₃As and Ph₃Sb. The kinetics of substitution for all except the last two ligands showed through the absence of an intercept in plots of pseudo-first-order rate constants versus excess nucleophile concentration that a reverse or parallel reaction does not contribute. The presence of a significant intercept for corresponding plots for the last two ligands indicated that a reverse solvolysis reaction is significant in those substitution reactions. The forward second-order rate constants did not depend markedly on the ligand but the effect of solvent (H₂O or CH₃OH) was not insignificant. However, the character of the organic-R group has a strong influence on the lability of the system. From this study together with results from other studies, the order of the kinetic *trans* effect is Et > PhCH₂ > Me > CH₂Cl > CF₃CH₂, according to the donor properties of the organic group. The absence of a marked dependence on nucleophile of the substitution reaction rates is normally suggestive of a similar and

dissociative mechanism. An excellent isokinetic relationship obtained from the thermal activation parameters tends to confirm the former suggestion, while the values of the activation volumes support a dissociative interchange mechanism, since typical values were between $+3$ and $+7 \text{ cm}^3 \text{ mol}^{-1}$. In the case of substitution of MeOH by Ph_3As in *trans*- $[\text{Co}(\text{Hdmg})_2(\text{Me})\text{MeOH}]$ the dependence on pressure of the rate constant for the reverse reaction (substitution of Ph_3As by MeOH) could be obtained leading to a volume of activation of $+15.9 \text{ cm}^3 \text{ mol}^{-1}$. For the forward direction the value of ΔV^\ddagger was determined to be $+10.6 \text{ cm}^3 \text{ mol}^{-1}$. These results permitted the drawing of a volume profile for the reaction (Fig. 10).

Obviously the reaction volume is negative. These volumes of activation were clearly much larger than those just cited above for other substituting ligands and would normally be thought to suggest the operation of a limiting D mechanism. The large value of ΔV^\ddagger for the reverse reaction was accounted for on the basis of the large partial molar volume of the leaving ligand Ph_3As . If the forward reaction actually proceeds by an I_d mechanism, the experimental volume of activation contains a term for the volume change for precursor formation as well as one for the interchange step itself. Thus the respective components are both unknown and thus complicating interpretation limiting any further detail to be introduced to the volume profile, and leaving the mechanism assignment less than unequivocal.

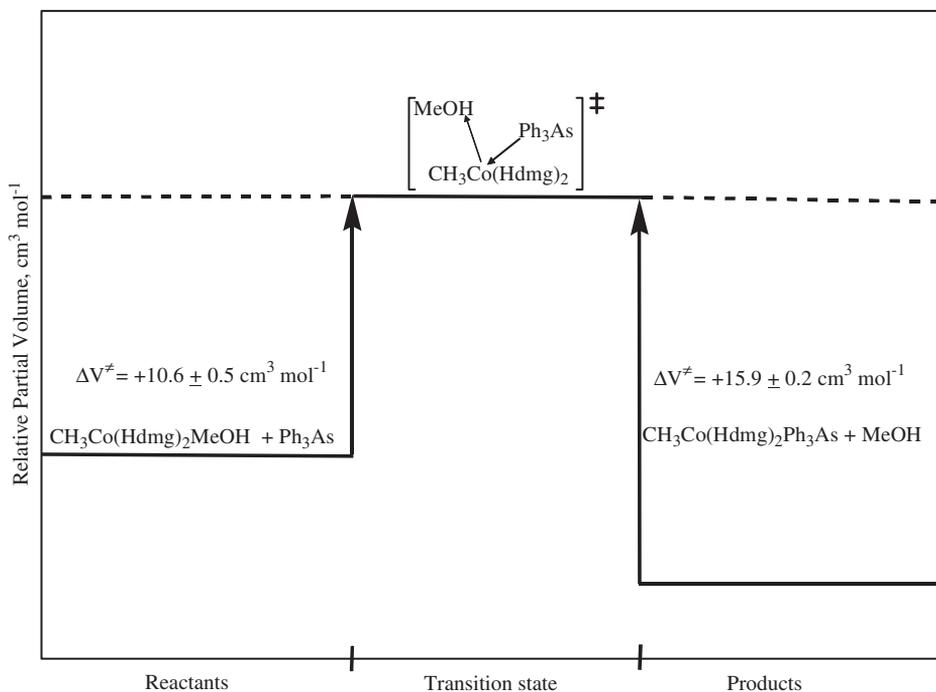
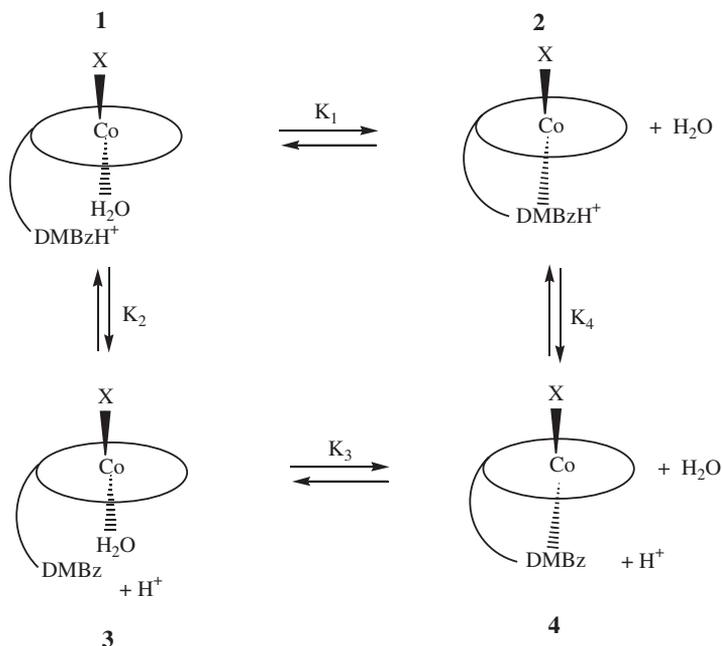


Fig. 10 Volume profile for the reversible reaction: *trans*- $[\text{Co}(\text{Hdmg})_2(\text{CH}_3)\text{MeOH}] + \text{Ph}_3\text{As} \rightleftharpoons \text{trans}-[\text{Co}(\text{Hdmg})(\text{CH}_3)\text{AsPh}_3] + \text{MeOH}$

The equilibria between the five- and six-coordinate species and possible adduct formation in Co(III)-corrinoids,¹⁹⁶ and the thermodynamic and kinetic properties of the base-on/base-off equilibration of alkyl cobalamins have been investigated.¹⁹⁷ In a closely related study the kinetics and thermodynamics of the corresponding equilibria and of the cyanation reaction in alkyl-13-epicobalamins have been examined.¹⁹⁸ In the first of these reports the pressure dependence of the UV/visible spectra of the five-coordinate (yellow)/six-coordinate (red) equilibrium for both methylcobalamin and vinylcobinamide was obtained.¹⁹⁶ Water is the additional ligand that gives rise to the five- to six-coordinate species conversion. The reaction volume could be obtained. It was identical for both equilibria ($\Delta V = -12.5 \pm 1.2$ and $-12.5 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ for the methyl and vinyl complexes, respectively). It was also remarkably close to the numerical value of -13 or $+13 \text{ cm}^3 \text{ mol}^{-1}$ advocated and generally accepted for limiting A or D mechanisms for the displacement of a water molecule.¹⁹⁹ Experiments with vinylcobinamide (five-coordinate) and dicyanocobinamide (six-coordinate) showed that adducts were formed with a selection of various added solutes, consistent with their places in the lyotropic series. It was suggested that these solute species are probably located in the hydrophobic cylinder surrounding the cobalt ion. The second report describes a study of the influence of the electronic nature of X on the base-on/base-off equilibration of a series of alkylcobalamins (XCbl). This is in effect a probe of the characteristic equilibrium property of cobalamins in which the axially coordinated DMBz is displaced by a water molecule (the base-off form) and protonated (Scheme 3).



Scheme 3.

A combination of equilibrium and kinetic measurements as a function of temperature, pressure and acid concentration was analysed and indicated that the base-off form of different XCbl species can possess different coordination. AdoCbl and ethylcobalamin are mainly five-coordinate, whereas the CF₃-, CN⁻- and H₂O-cobalamins have little base-off form and exist mainly as six-coordinate species. When X = CH₃, CH₂Br or CH₂CF₃ there is an equilibrium mixture of the five- and six-coordinate species. Evidence for an acid-catalysed dechelation (of DMBz) pathway was provided. Two derivatives (NCCH₂ and CN⁻) of the epimer obtained by epimerisation at C13, in which the *e*-propionamide side chain adopts an upwardly axial configuration, have been the subject of an extensive study of the cyanation reaction.¹⁹⁸ From results obtained by varying the cyanide concentration, temperature and pressure, it was clear that epimerisation has a sensitive influence on the kinetics of displacement of the DMBz moiety, first by water and then by the cyanide ion. The rate of substitution was reduced compared with an alkylcobalamin. Displacement of DMBz at high cyanide concentration showed saturation kinetics, and the activation parameters, ΔS^\ddagger and ΔV^\ddagger for the limiting rate constant are $+77 \pm 4$ and $+82 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$, and $+13.3 \pm 1.0$ and $+14.8 \pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$ for the NCCH₂ and CN⁻ epimers, respectively. These values were interpreted as evidence for a limiting D mechanism.

On the basis of significantly positive entropies and volumes of activation a limiting D mechanism was also proposed for the kinetics of displacement of DMBz by CN⁻ in XCbl where X = β -NCCH₂ or CN⁻.²⁰⁰ In these systems saturation kinetics were also observed at high cyanide ion concentrations. An overall appraisal of mechanistic features for these reactions was included as part of a reinvestigation into some of the apparent ambiguities in the literature. Further attempts to establish a consistent, comprehensive view of substitution reactions of Co(III) compounds that have analogy with the more direct bio-relevant compounds involved studying the kinetics of substitution reactions of various cobaloximes.²⁰¹ The kinetics of axial water substitution by cysteine in six different cobaloximes (*trans*-RCo(Hdm-g)₂(H₂O) with R = cyclo-C₅H₉, CH₃CH₂, CH₃, C₆H₅CH₂, C₆H₅ and CF₃CH₂) in aqueous solution, have been investigated. While five-coordinate species have been inferred from results of studies on coenzyme B₁₂ in aqueous medium and on alkylcobaloximes in non-coordinating solvents, the evidence, largely on the basis of the magnitude of ΔV^\ddagger , was that the mechanism is dissociative interchange, and implying the absence of five-coordinate species. The absence of a linear isokinetic plot suggested mechanistic variation and since the value obtained for ΔV^\ddagger for the CF₃CH₂ derivative was $0 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$, it was concluded that an interchange mechanism operated in this case. It could also be concluded that the activation parameters are influenced by a combination of electronic and steric factors.

A perspective report emphasised the key role of the application of pressure in kinetic studies in bringing clarity to understanding the mechanism of substitution reactions of cobalamins.¹⁹³ The effect of various alkyl substituents in the *trans* position on the kinetic, thermodynamic and ground-state properties has been studied. Cobalamins featuring in these studies were cyanocobalamin (vitamin B₁₂), aquacobalamin and the complex formed when the cyano or water ligand is replaced

by the 3'-deoxyadenosyl moiety. This report recounted the use of ΔV^\ddagger in mechanistic diagnosis in this field. It also pointed out the role the effect of pressure on the UV/visible spectra of various cobalamins had in demonstrating the influence of the alkyl group in controlling the equilibrium between the five- and six-coordinate species, relating to these species potential participation in ligand substitution processes. It became clear that the nature of the cobalt-carbon bond and the character of the substituent supplying the carbon atom to that bond are vitally important. Applying UV/visible and ^1H NMR spectroscopies, including the determination of ΔV^\ddagger ($= -4.5 \text{ cm}^3 \text{ mol}^{-1}$) for the reaction of co-enzyme B_{12} with cyanide ion, indicated that the rate-determining step involves solvent assisted heterolytic cleavage of the cobalt-carbon bond.²⁰²

As noted above, the cobalamin analogue, in which DMBz has been replaced by imidazole (CN(Im)Cbl), has been prepared.¹⁹¹ Experiments with this compound allow among other aspects a test of the effect of the steric bulk of the nucleotide base on the upward folding of the corrin ring. Furthermore, the properties of the system regarding substitution can be compared with those of similar systems. A systematic study of the kinetics of substitution of imidazole by cyanide was conducted, and the kinetics and thermodynamics of the acid-base chemistry of CN(Im)Cbl were investigated thoroughly. The cyanide ion substitutes imidazole in the α -position more slowly than it substitutes DMBz in cyanocobalamin. At high cyanide ion concentration saturation kinetics are exhibited yielding activation parameters, $\Delta H^\ddagger = 111 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = +97 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta V^\ddagger = +9.3 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$. The reverse reaction in which the coordinated cyanide is displaced by the dangling chelate is notably faster for CN(Im)Cbl, also consistent with an I_d mechanism. Spectrophotometric titrations led to the result that the $\text{p}K_{\text{base-off}}$ equilibrium is about one unit higher than the value determined earlier for cyanocobalamin. This has its origin in the different basicities of the nucleotide unit to which the Im and DMBz groups are attached. The kinetics of the base-on/base-off reaction indicated an acid catalysed pathway.

Contemporaneously, studies of ligand substitution of relevant organometallic model systems for coenzyme B_{12} were under investigation. As alluded to earlier, mechanistic clarity was sometimes absent and further studies on appropriate systems could usher in mechanistic transparency. Accordingly the kinetics of ligand substitution reactions of octahedral $\text{trans}[\text{Co(III)(en)}_2(\text{Me})\text{H}_2\text{O}]^{2+}$ (en = ethene 1,2-diamine) were studied.²⁰³ The cyanide and imidazole (Im) nucleophiles (L) displaced the coordinated water molecule *trans* to the methyl group to form the six-coordinate complex $\text{trans}[\text{Co(en)}_2(\text{Me})\text{L}]$ (charge omitted). The reactions were rapid requiring employment of the s.f. method. Absorbance changes in the near UV and in the visible regions were used to monitor the substitution reactions spectrophotometrically. The kinetics of the reactions with cyanide ion and with ImH as a function of pressure gave rise to volumes of activation of $+7$ and $+4.7 \text{ cm}^3 \text{ mol}^{-1}$, respectively. These values were regarded as compatible with an I_d mechanism in which the entering ligand becomes weakly bound in the transition state. The stability constant for the reaction with cyanide was more than an order of magnitude higher than that for substitution of imidazole, a fact that made possible the determination of the

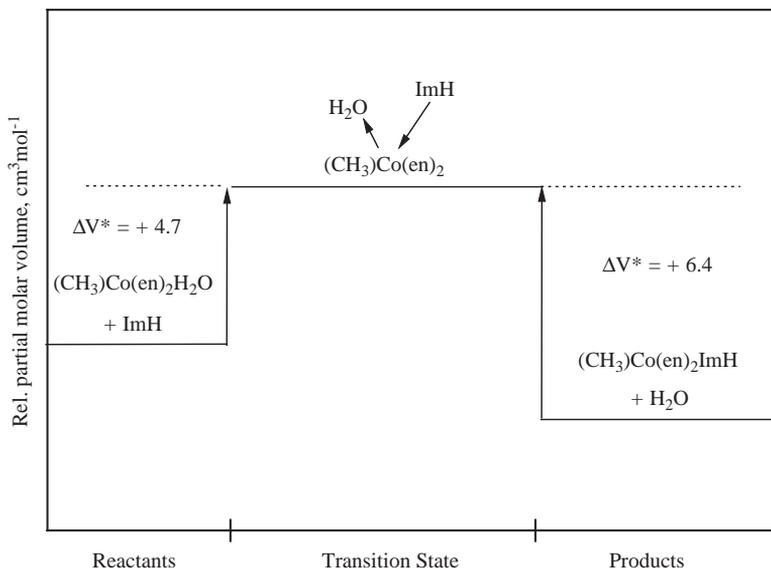


Fig. 11 Volume profile for the reaction of imidazole with $\text{trans}[\text{Co}(\text{en})_2(\text{Me})\text{H}_2\text{O}]^{2+}$ in aqueous solution at 10°C .

volume of activation for the reverse reaction in the latter case. The intercepts of plots of the observed first-order rate constants versus excess imidazole concentration at different pressures were utilised for that purpose. In turn the volume profile for the forward and reverse reactions of imidazole substitution could be constructed and is displayed in Fig. 11.

The dissociative nature of the reaction is evident from the magnitudes of the volumes of activation ($+6.4 \text{ cm}^3 \text{ mol}^{-1}$ for the substitution of ImH by H_2O). As in another report above the certainty of I_d character is clouded by the fact that the values of ΔV^\ddagger are composites of a precursor complex component and a contribution from the interchange step itself. A full D mechanism could not be categorically ruled out based on the properties of the system, and since the precursor formation step could contribute a negative volume term. Nevertheless a dissociative interchange mechanism was proposed as the more likely and a thorough discussion of mechanistic features, available at the time, of related systems was included.

In a following report equilibrium, kinetic and leaving group effects on ligand substitution in the same $\text{Co}(\text{III})$ -ethene 1,2-diamine complex and in the corresponding $\text{trans}[\text{Co}(\text{III})(\text{en})_2(\text{Me})\text{NH}_3]^{2+}$ were investigated.²⁰⁴ The ligands employed were CN^- , SCN^- , N_3^- and NH_3 , and these displace the coordinated water or ammonia molecules *trans* to the methyl group. The most important aspect of this report that is pertinent here is the reaction of NH_3 with the aqua complex, $\text{trans}[\text{Co}(\text{en})_2(\text{Me})\text{H}_2\text{O}]^{2+}$, since kinetics experiments at elevated pressures were conducted. The kinetics results at ambient pressure established a second-order reaction, with the condition of NH_3 in excess, pseudo-first-order (k_{obs}) in practice. From the slope and intercept

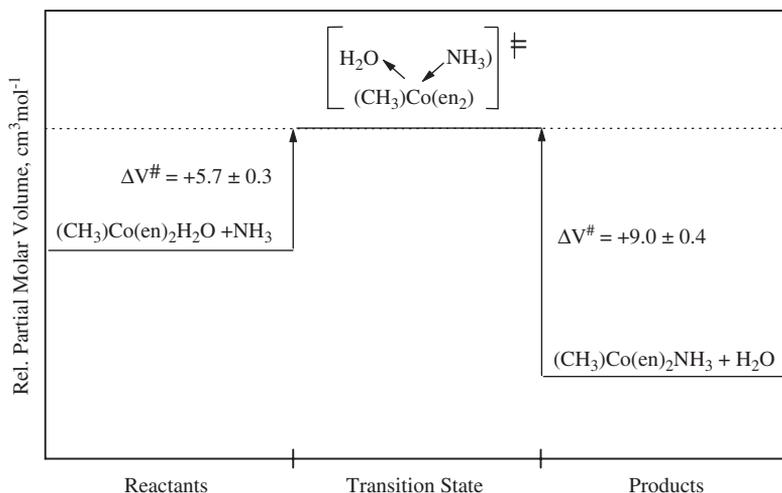


Fig. 12 Volume profile for the reaction of NH_3 with $\text{trans-}[\text{Co}(\text{en})_2(\text{Me})\text{H}_2\text{O}]^{2+}$ in aqueous solution at 5°C .

of plots of k_{obs} versus $[\text{NH}_3]$ the rate constants of the forward and reverse reactions, respectively, could be acquired. Volumes of activation from the pressure dependence of kinetic parameters were $+5.7$ and $+9.0 \text{ cm}^3 \text{ mol}^{-1}$ for the substitution of H_2O , and the reverse aquation reaction, indicating a transition state of greater partial molar volume than reactant or product states. This is depicted in Fig. 12.

This volume profile is qualitatively similar to that in Fig. 11 and not very different quantitatively, indicating similarity in the mechanism, perhaps not unexpected for similar reactions. A potential advantage of the en model system, it was pointed out, was the two somewhat flexible chelate systems. It had been suggested that this property could be important for the biological activity of the coenzyme.²⁰⁵ The substitution of NH_3 by SCN^- , N_3^- and CN^- in $\text{trans-}[\text{Co}(\text{en})_2(\text{Me})\text{NH}_3]^{2+}$ proceeded via the intermediate aqua complex such that aquation of the amine complex became the rate-determining step at high entering ligand concentration.

Rhodium and iridium

Substitution reactions of dimethylglyoximato complexes have also been studied for the transition metal second row analogue rhodium(III), specifically substitution of water in $\text{trans-}[\text{Rh}(\text{Hdmg})_2\text{R}(\text{H}_2\text{O})]$ where R is CH_3 , CH_2Cl or CH_2CF_3 .²⁰⁶ These reactions had been studied earlier²⁰⁷ at ambient pressure but a more definitive proposal for the mechanism was sought. The lability of the coordinated axial water molecule has been shown to be influenced by the nature of the R group and by the equatorial chelating ligands. The entering ligands were neutral (pyridine, thiourea (TU) or TMTU) or mono-anionic (I^- , SCN^- or N_3^-). It was established that the rate constant for the substitution reaction was not very sensitive to the nucleophilicity of the incoming ligand, and together with the values of the thermal activation parameters

suggested a dissociative interchange mechanism. Upon analysing the kinetics results, except for the iodide ion all incoming ligands provided no evidence of an observable back reaction. The dependence on pressure of the rate constants for the substitution reactions yielded positive values of the volume of activation for $R = \text{CH}_3$, py and TMTU as entering ligands, whereas the values for $R = \text{CH}_2\text{Cl}$ and CH_2CF_3 were negative (TU as the incoming ligand). The volume of activation for the aquation of the iodide complex species was also positive. The reason that the faster substitution reactions ($R = \text{CH}_3$) exhibit positive ΔV^\ddagger values while the slower reactions ($R = \text{CH}_2\text{Cl}$ or CH_2CF_3) proceeded with a rate acceleration with increasing pressure could have its origin in the *trans*-labilising effect on the Rh–O bond distance. For Rh–py complexes the bond lengths *trans* to the R group progressively decreases for $R = \text{CH}_3$, CH_2Cl , CH_2CF_3 and a parallel situation probably prevails for *trans*-[Rh(Hdmg)₂R(H₂O)] species. Hence the mechanism is electronically tuned, changing from an I_d mechanism for the faster reactions to an I_a mechanism for the slower reactions. Other examples of substitution reactions in which a metal–carbon bond influences reactivity are covered in the section on platinum chemistry. A volume profile could be drawn for the reaction of the iodide ion and the reverse aquation reaction illustrating the increased volume of the transition state relative to reactant and product states (Fig. 13).

The more positive volume of activation ($+6.3 \text{ cm}^3 \text{ mol}^{-1}$) for the dissociative release of the iodide ion than for release of the water molecule ($+2.1 \text{ cm}^3 \text{ mol}^{-1}$) was considered to arise from the larger partial molar volume of the iodide ion and the reduction in electrostriction of the complex ion.

The lability of water molecules in the η^5 -organometallic complexes $\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3^{2+}$ and $\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_3^{2+}$ and the mechanism of water exchange with bulk solvent water molecules were discussed in the previous section.¹⁵⁹ A subsequent study in which the kinetics of substitution of a water molecule in these species by several ligands (L) at

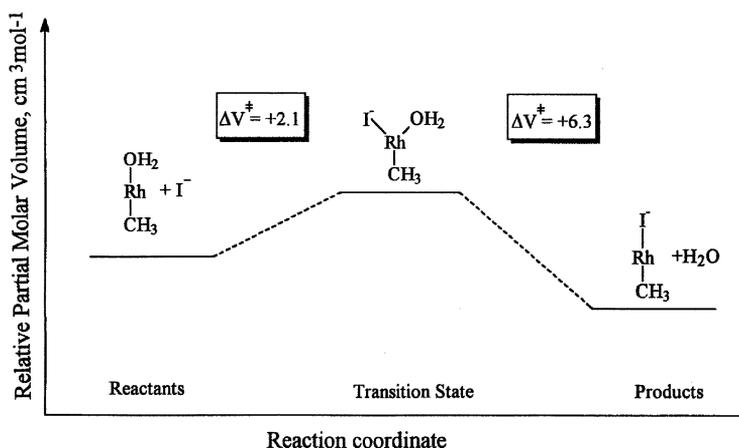


Fig. 13 Volume profile for the reaction of iodide ion with *trans*-[Rh(Hdmg)₂Me(H₂O)]²⁺ in aqueous solution at 9°C.

various concentrations, temperatures and pressures has brought insight into the mechanism of substitution and allowed the development of volume profiles.²⁰⁸ The ligands were anionic (Cl^- , Br^- , I^- , SCN^-) or neutral (4-cyanopyridine, nicotinamide, pyridine, TU and dimethylsulphide (DMS)) which would allow the exploration of the significance, if any, of charge upon the entering ligand. The substitution reactions were monitored by s.f. spectrophotometry. Conditions for monitoring the kinetics could be selected since series of spectrophotometric, potentiometric and NMR pH titrations had been carried out to establish the species present in a range of conditions. For both anionic and neutral ligands the rhodium compound forms only mono-substituted complexes, $\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_2\text{L}^{2+/+}$ while both mono- and bisubstituted complexes are formed with the iridium compound when L is neutral. Stability constants that were determined were highest for two sulphur-containing neutral ligands. As noted earlier, coordination of the Cp^* ligand gives rise to extreme labilisation of the coordinated water relative to the corresponding hexa-aqua ions and this effect gives rise to rapid substitution reactions. The second-order rate constants for formation of the mono-substituted complexes are higher for the anionic ligands, but except for the SCN^- ligand range over little more than an order of magnitude, and are very similar for the rhodium and iridium species. A method of approach to determine the reaction mechanism involves correcting the second-order rate constant for outer-sphere complex formation and a statistical factor to yield the rate constant for the interchange (ligand for water) step. These rate constants were not highly dependent on the nature of L and were in the same general range as the rate constants for water exchange, thus suggesting an interchange mechanism of dissociative character. Although the second-order rate constants and the calculated interchange rate constants do not vary widely the variation of them was examined with respect to a scale of nucleophilicity for both the anionic and neutral ligands and also with the basicity of the pyridine ligands. The nucleophilicity discrimination factor was well below that found for typical associative mechanisms, and on this basis an associative mechanism of substitution could be excluded. Further mechanistic assignment could be inferred from the kinetic parameters derived from high pressure measurements. The volumes of activation for the forward substitution and reverse aquation reactions were determined, and thus the reaction volumes could be calculated and volume profiles developed for the mono-substitution process. In all cases the volume of the transition state was larger than that of the reactant state (triqua species and the ground-state ligand), further supporting the proposal of a dissociative mode of activation. The reaction volumes for the charged ligands are positive since the anation reaction results in loss of electrostriction. The reverse (aquation) reaction is accompanied by charge creation, an increase in electrostriction, a volume change that surpasses the volume increase due to partial bond breakage since the volumes of activation are negative. It has also been noted that the volumes of activation in the forward direction are modest values. For example, when $\text{L} = \text{Cl}^-$ and Br^- , they are $+1.1$ and $+0.8 \text{ cm}^3 \text{ mol}^{-1}$ respectively, for the rhodium triqua species, and that these could mask a volume contraction of the spectator water molecules around the small d^6 ion, that may occur as the transition state is reached. It was suggested further that the actual bond lengthening of the

M–OH₂ bond to reach a dissociative transition state is much smaller than would be the case for the ground-state labilisation arising from the effect of the presence of the Cp* moiety. Taken together these factors do not permit the exclusion of a limiting D mechanism. The volume profiles for reactions of chloride ion, bromide ion, 4-cyanopyridine (py-CN) and nicotinamide (py-nia) with Cp*Rh(H₂O)₃²⁺ are displayed in Fig. 14.

For the iridium compounds the volumes of activation for the anionic ligands are about +4 cm³ mol⁻¹. When the ligands are neutral the reaction volumes are small and sometimes negative and sometimes positive (an exchange of one neutral ligand for another and absence of changes in electrostriction). But the volume of the transition state is always larger than that of the reactants or products, indicative of a dissociative mechanism. The sensitivity of the kinetic parameters to the nucleophilicity of the sulphur-containing ligands for the reaction with the iridium compound raised speculation that an associative activation mode occurs. However, the activation volume for the complex-formation reaction of SCN⁻ with Cp*Ir(H₂O)₃²⁺ was clearly positive, further supporting an I_d or even a D mechanism. Substitution of a second water molecule by a neutral ligand is slower by an order of magnitude indicating that the labilisation effect of Cp* is markedly reduced.

Subsequently a study of the kinetics and mechanism of water substitution on half-sandwich iridium(III) aqua cations, Cp*Ir(A-B)(H₂O)^{2+/+} (A-B = bidentate N,N or N,O ligand) by several monodentate ligands was reported.²⁰⁹ The A-B ligands included the D/L proline anion, the picolinic acid anion, 2,2'-bipyridine and 1,10-phenanthroline. Monodentate entering ligands included pyridine, TU, DMS and the anions Br⁻, I⁻, SCN⁻, N₃⁻ and NO₂⁻. Second-order rate constants for substitution by pyridine in several aqua cations were sensitive to the nature of A-B with a range of values of over 500, with the singly charged cations reacting more rapidly than the doubly charged ones. Charge was found to be not the only rate-determining factor. When experimentally accessible the rate of the reverse, aquation reaction was not dramatically affected by the nature of A-B. Water substitution by TU and DMS at various cations is much faster for the singly charged cations than it is when A-B = phen. For a given cation the magnitude of the substitution rate constants follows the order TU > DMS > py. In general water substitution by anionic ligands is faster than it is for neutral ligands. Analysis of the data showed a rather weak dependence on the nucleophilicity of the entering ligand. The activation parameters obtained for the reactions of three mono-aqua cations with TU were reasonably decisive in terms of mechanistic assignment. Specifically the modestly positive volumes of activation (+2.3 to +7.4 cm³ mol⁻¹) point to a dissociatively controlled interchange mechanism. It was suggested that the increase in these values corresponded to an increase in the substitution rate constants; this may point to progressively more dissociative character. However, these values of ΔV[‡] are in line with those for the water substitution by ligands on the triaqua complex, Cp*Ir(H₂O)₃²⁺, also assigned an I_d mechanism. These reactions are all several orders of magnitude faster than water exchange and ligand substitution on hexa-aqua iridium(III) where the mechanism was assigned I_a based on the negative volumes of activation. However, the pronounced labilisation induced by the Cp* moiety stimulates a cautionary

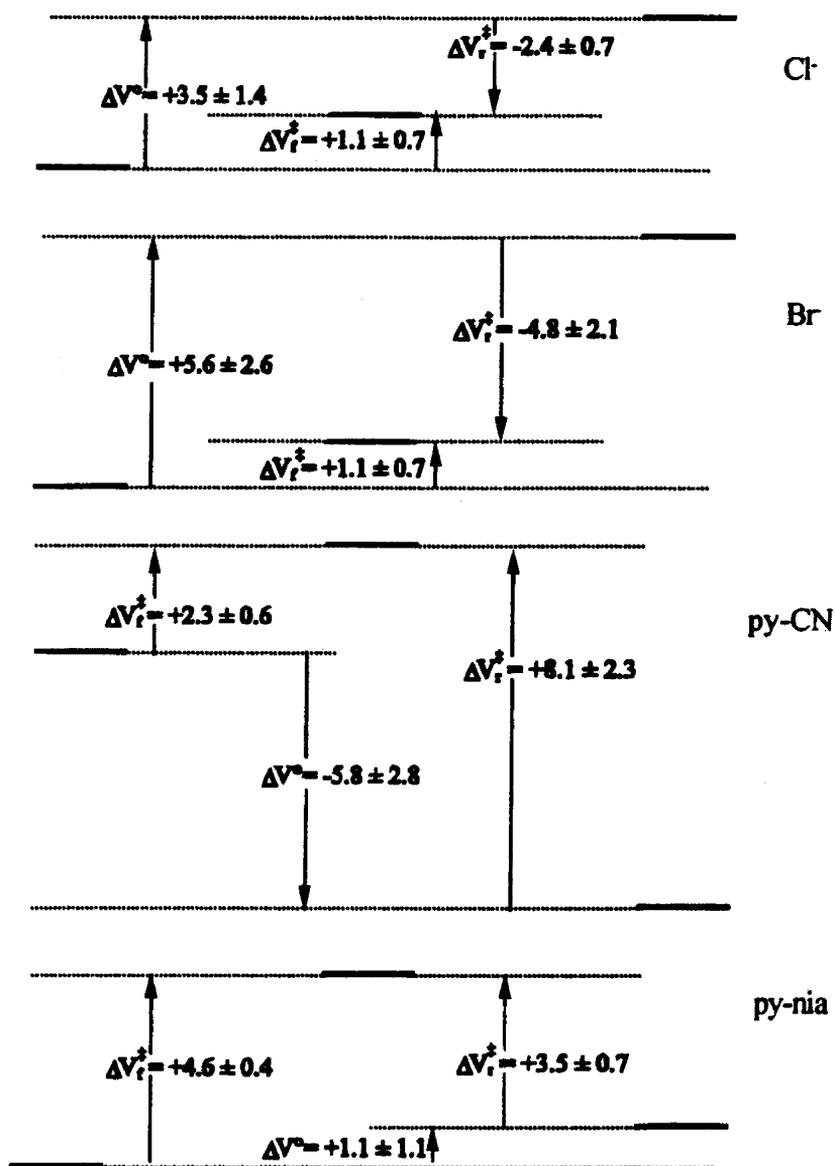
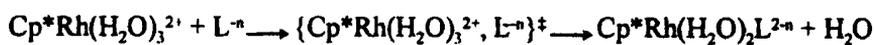


Fig. 14 Volume profiles for reactions of chloride ion, bromide ion, 4-cyanopyridine (py-CN) and nicotinamide (py-nia) with Cp^{*}Rh(H₂O)₃²⁺ in aqueous solution at 25 °C.

note that since, as a consequence, ground-state lengthening of the Ir–OH₂ bond would be expected, then a lesser degree of bond breaking upon reaching the transition state would ensue in a substitution reaction. Hence a modest ΔV^\ddagger alone does not entirely rule out a D mechanism.

Tungsten

This section also includes reactions of organomolybdenum systems where these are related to comparable reactions of tungsten-based compounds. Several studies of substitution kinetics of Group 6 metal hexacarbonyls have shown that the reactions normally follow a two-term rate law representing parallel reaction pathways, one of which involves the incoming ligand in the transition state and the other does not.²¹⁰ The pathway involving associative attack provides the dominant path for Mo or W compounds.²¹¹ Many pentacarbonyl derivatives [M(CO)₅(L)], including [Mo(CO)₅(py)], [Mo(CO)₅(4Mepy)], [Mo(CO)₅(4CNpy)] and [W(CO)₅(py)] also exhibited kinetic characteristics of a limiting D mechanism.^{212,213} However, activation volumes for reactions of this type were smaller than might be expected, being in the range of 0 to +5 cm³ mol⁻¹.²¹⁴ Substitution at tetracarbonyl derivatives [Mo(CO)₄(L)₂] and [Mo(CO)₄(LL)] (L = py, or 4Mepy, LL = bpy, phen or dab) was also considered to take place by a D mechanism, despite the small positive values of the volumes of activation. The entropies of activation were distinctly positive. The first-order rate constants were independent of the concentration of the entering bidentate ligand, a result that means either bond cleavage to produce a five-coordinate intermediate or ring closure of a ring opened product species was rate determining. Therefore all the evidence except the small positive volumes of activation pointed to a D mechanism. The explanation resided in two possibilities. It was noted that the rate of the rate-determining step was strongly dependent on solvent polarity in the series hexane, toluene, 1,2-dichloroethane. Solvent polarity increases with increasing pressure and this was argued to cause an increase in rate constant with pressure that reduces the actual rate retardation intrinsic to the reaction. This results in a volume of activation of 5 cm³ mol⁻¹ lower than it otherwise would be in the absence of the effect of pressure on solvent polarity. Alternatively, it was proposed that an internal rearrangement of the five-coordinate intermediate might occur resulting in a volume collapse that is smaller than expected for a D mechanism.

In order to further extend this work to similar tungsten compounds, a study of the kinetics of substitution at *cis*-tetracarbonyl bis(4-methylpyridine)tungsten(0) in toluene was undertaken.²¹⁵ Incoming ligands employed were bpy, phen, 5-NO₂phen and bipym = 2,2'-bipyrimidine, and they were present in excess concentration over that of the tungsten compound. First-order rate constants were obtained from monitoring the appearance of [W(CO)₄(LL)] spectrophotometrically. Analysis of the dependence of rate constants on nucleophile concentration and on the rate retardation pattern when the leaving group was added to the reacting system led to the conclusion that a limiting D mechanism was in operation. Further kinetics experiments with phen as the entering ligand and applying pressure gave rise to an activation volume of +8 cm³ mol⁻¹, thus supporting firmly a limiting dissociative mechanism.

Rhenium

Following the report cited above¹⁶⁵ that covered primarily the water exchange kinetics on *fac*-[(CO)₃Re(H₂O)₃]⁺, an extensive study of the kinetics of ligand substitution of coordinated water by N- and S-donor ligands (pyrazine (pyz), tetrahydrothiophene (THT) and dimethylsulphide (DMS)) has been described.²¹⁶ To avoid complications that would ensue if the monohydroxy species of the tricarbonyl rhenium species were present, appropriate conditions of a range of acidity were chosen. The kinetics measurements were to be conducted at elevated pressures, therefore experiments (spectrophotometry and ¹H NMR spectroscopy) were performed to assess the effect of pressure upon the acidity constant of pyrazine. Depending on the ligand concentration the product of reaction was the mono-complex [(CO)₃Re(H₂O)₂(pyz)] or in addition the binuclear complex [(CO)₃(H₂O)₂Re(μ-pyz)Re(H₂O)₂(CO)₃]²⁺. The kinetics of the substitution reaction at variable pressure were studied under conditions where only one of the water molecules was substituted. Volumes of activation of +5.4 and +7.9 cm³ mol⁻¹ were derived for the forward and reverse reactions, respectively. Corresponding experiments for substitution of water by THT yielded volumes of comparable magnitude but of opposite sign (-6.6 and -6.2 cm³ mol⁻¹ for the forward and reverse reactions, respectively). All three water molecules of [(CO)₃Re(H₂O)₃]⁺ can be displaced by DMS, and the equilibria and kinetics parameters have been obtained for each of the successive substitution reactions. Remarkably from the variable-pressure kinetics measurements the volumes of activation for each step have been derived enabling the development of a volume profile containing the volume change information for each reaction step. In all cases the volumes of activation were negative quantities (Fig. 15).

An initial attempt to assign the reaction mechanism for these complex-formation reactions was based on consideration of the nucleophilicity of the incoming ligands, three in this study and others reported earlier,¹⁶⁵ in terms of basicity and polarisability relative to the calculated interchange rate constant. It was debated whether the difference in solvation of the ligands (pyz is hydrophilic and THT and DMS are more hydrophobic) yielded a significant contribution to the volumes of activation. It was concluded from the reaction volumes that this was not a prominent factor, and mechanistic enlightenment emerged from deciding that the substitution could operate in dual modes. With hard nucleophiles, such as O- and N-donors an I_d mechanism prevails, whereas the affinity of soft S-nucleophiles for the soft rhenium centre leads these ligands to become part of an associative transition state, according to an I_a mechanism. The successive substitutions of the three DMS ligands show a progressive decrease in the rate constant, a trend related to increased steric hindrance on the MC. This is confirmation of an associatively activated substitution. At first sight the progressive increase in the equilibrium constant for each successive DMS ligand appears contradictory to the kinetics trend. Upon analysing data for formation of the corresponding TU complexes it was reasoned that the progressively increasing affinity arose from a softening of the MC by coordinated ligand(s).²²⁰

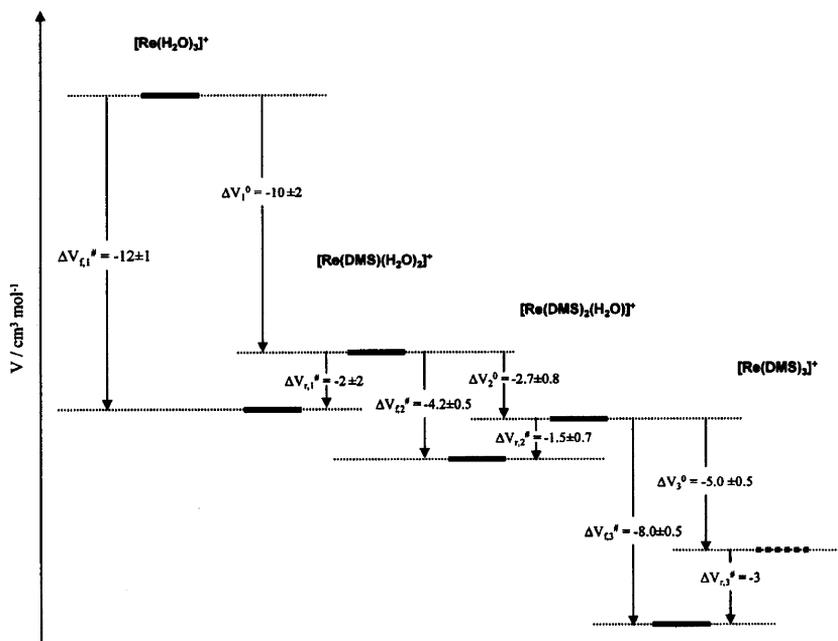
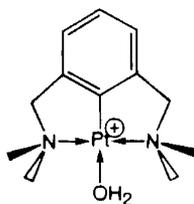


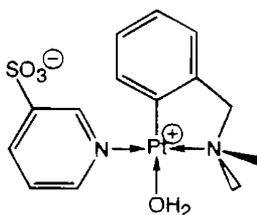
Fig. 15 Volume profile for the reaction of DMS with $[(\text{CO})_3\text{Re}(\text{H}_2\text{O})_3]^+$ in aqueous solution at 25°C .



Scheme 4.

Platinum

Substitution reactions of platinum(II) complexes containing one or more metal carbon bond(s) have a long history.²¹⁷ Interest in such complexes and their reactivity is associated with their function as catalysts in synthetic procedures and in environmental applications. One important characteristic is the kinetic *trans* effect; this is ascribed to the labilisation of a *trans*-positioned group caused by a C-bonded ligand,²¹⁸ typically alkyl or aryl. In a mechanistic study in which kinetics measurements at elevated pressures were employed, cyclometallated Pt(II) complexes were used.²¹⁹ The complex shown in **Scheme 4** is water-soluble permitting the kinetics of substitution by a wide range of nucleophiles to be studied in aqueous solution.

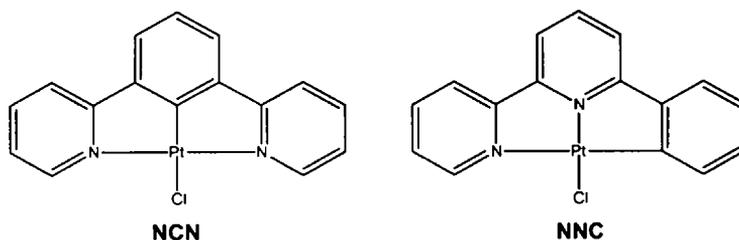


Scheme 5.

The reactions were rapid requiring s.f. techniques. Large negative values of the entropy and volume of activation were obtained for the reaction of TMTU with the cyclometallated compound, and were interpreted to indicate an associative substitution mechanism. The same conclusion had been reached in an earlier study of the substitution of the water molecule from the zwitterionic-Pt compound as shown in Scheme 5.²²⁰

The marked increase in lability of the former compound relative to the zwitterionic compound can be attributed to the σ -donicity of the second chelating dime-thylamino group and/or the increased chelation effect of the terdentate ligand.

Some uncertainty arose regarding the mechanism of substitution reactions of complexes of the type *cis*-[PtR₂S₂] with R = Me, Ph and S = DMSO, thioether.²²¹ Substitution reactions for this type of Pt(II) complex have usually followed an associative pathway. However, convincing evidence for a dissociative mechanism was presented for reactions in which bidentate ligands functioned as the entering nucleophile. It was proposed that mechanistic clarity might follow if monodentate ligands were employed so that the successive substitution of the two labile solvent molecules could be monitored kinetically. Accordingly a kinetics study of the substitution reaction in which the pyridine ligand replaces DMSO in *cis*-[PtMe₂(DMSO)₂] was undertaken. The solvent was toluene and this allowed a systematic variation of the concentration of the leaving group by addition of DMSO. Analysis of the results revealed that in forming the monopyridine complex two reaction paths, one dissociative and one associative, were followed. The former was suppressed if the concentration of added DMSO was more than 40-fold in excess. The parallel path was supported in its associative nature by the volume of activation of $-11.4 \text{ cm}^3 \text{ mol}^{-1}$, at high saturating pyridine concentration. This value contains the volume change for the formation of the precursor complex and the substitution step itself, where substitution is the dominant contributor. Study of the entry of the second pyridine molecule indicated two parallel paths leading to the product. One involves the complete dissociation of the second DMSO molecule before the pyridine molecule binds and the second involves a synchronous substitution of pyridine for DMSO. The volume of activation determined for the formation of the bispyridine complex comprises contributions from both of these processes. For the former of the two steps the volume of activation must be distinctly positive, whereas for the latter step an associative activation mode can be expected contributing a negative component to the volume of activation. Therefore the measured value of $+1.9 \text{ cm}^3 \text{ mol}^{-1}$



Scheme 6.

was said to represent a minimum value. The results were considered in terms of other reactions of Pt(II) complexes containing two *cis* metal–carbon bonds and also considering the *trans* effect on the lability of ligands. However, at the time of writing it was opined that the substitution mechanism of such complexes was not yet fully understood.

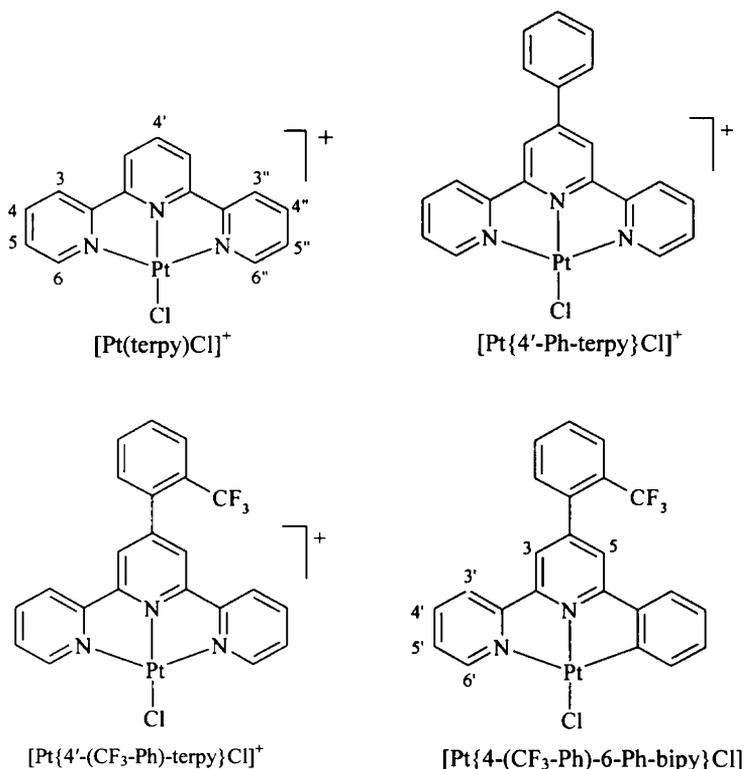
Since these earlier studies demonstrated the mechanistic diagnostic value of knowledge of the volume of activation, a wide-ranging study of several cyclometallated compounds analogues of platinum(II) terpyridine (terpy = 2,2':6',2''-terpyridine)/chloro complexes has been undertaken.²²² Structures were determined by crystallographic methods and reactivities were investigated by ligand substitution kinetics measurements. TU, DMTU and TMTU were employed to displace the chloro ligand from [Pt(N–N–C)Cl] and [Pt(N–C–N)Cl] where N–N–CH is 6-phenyl-2,2'-bipyridine and N–CH–N is 1,3-di(2-pyridyl)benzene. The complexes are illustrated in Scheme 6.

One principal objective in this and related studies is to examine the relationship between σ -donor and π -acceptor effects in Pt(II) chemistry. A much higher reactivity observed for the N–C–N compound was reflected in a 20 kJ mol^{-1} lower enthalpy of activation than for the N–N–C compound. This was explained by citing the influence of the *trans* phenyl group in destabilising the ground state, thus facilitating cleavage of the leaving group to Pt bond. For the N–N–C compound the activation enthalpy trend was $\text{TMTU} < \text{DMTU} \approx \text{TU}$ whereas for the N–C–N compound the relationship was $\text{TMTU} < \text{DMTU} < \text{TU}$, a sequence not in accord with expected reactivity trends. It was concluded that differences in entropies of activation were responsible for the observed steric retardations. For each of the three TU entering ligands negative volumes of activation were obtained for both platinum compounds. A volume contraction occurs upon forming the transition state arising from the bond formation by the entering nucleophile, although this is partly offset by the geometry changing from square planar to trigonal bipyramidal. In the case of the N–C–N compound the platinum–ligand bonds of the entering and leaving ligands are longer owing to the *trans* influence. Thus the observed ΔV^\ddagger values were less negative for reaction of the N–C–N compound than for the reaction of the N–N–C compound reaction where the corresponding bonds are shorter. From these results and abundant literature on substitution reactions at Pt(II) it was concluded that the magnitude and direction of the *cis* effect (as compared to the *trans* effect of the same ligand) depend on the σ -donor strength, π -acceptor ability

and the steric property of the *cis* ligand. The relative magnitudes of these factors and their subtle interplay have consequences for reactivities of these and related compounds.

In a related investigation the roles of chelate substituents and the *cis* effect on the rate of ligand substitution at (Pt(N–N–N) and Pt(N–N–C) centres were explored in methanol solution.²²³ The terdentate ligands were terpyridine, 4'-Ph-terpy, 4'-(2'''-CF₃-Ph)-terpy and 4'-(2'''-CF₃-Ph)-6-2,2'-bpy and the remaining position was occupied by a chloro ligand (Scheme 7).

The rates of substitution of the latter ligand by TU, DMTU and TMTU were followed as a function of nucleophile concentration, temperature and pressure by s.f. spectrophotometry. The reaction was first order in both platinum complex and nucleophile concentrations. From the form of the rate law and the negative entropies and volumes of activation it was concluded that the mechanism is an associatively activated substitution. It prevailed that substitution in the terpy parent ligand did not affect significantly the kinetic parameters. The reaction was slower when a carbon σ -donor was in the *cis* position than when an N σ -donor occupies this position, indicating a different situation from the effect of a Pt–C bond in the *trans* position.



Scheme 7.

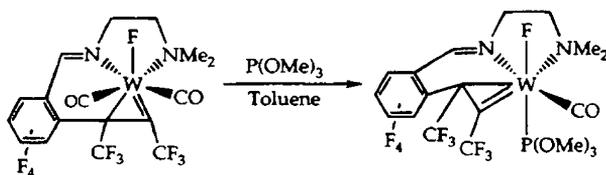
The subject of homogeneous hydrocarbon C–H bond activation and functionalisation with platinum compounds has been authoritatively reviewed, and the review contains literature reports up to and including most of 2003.²²⁴ A noteworthy sample report from this account presented evidence for an associative mechanism for benzene substitution at a platinum(II) centre.²²⁵ The mechanism specifically addressed was that for the first key step in the multistep catalytic cycle of a Shilov-type system.²²⁶ The reaction of the platinum(II) methyl cation $[(N-N)Pt(CH_3)(solv)]^+$ ($N-N = ArN = C(Me)C(Me) = NAr$, $Ar = 2,6-(CH_3)_2C_6H_3$, $solv = H_2O$ or $TFE = CF_3CH_2OH$), with benzene in TFE/ H_2O mixtures afforded the platinum(II) phenyl cation $[(N-N)Pt(C_6H_5)(solv)]^+$. To resolve the mechanism of the mode of entry of benzene into the coordination sphere a high pressure kinetics study was undertaken, monitoring UV/visible absorbance changes. The reaction was accelerated by pressure yielding a negative volume of activation. This parameter contains a reaction volume term for displacement of the coordinated water by TFE and a second term for the volume of activation for the activation of benzene by the TFE–solvento complex. The latter term could be determined to be $-9.5 \text{ cm}^3 \text{ mol}^{-1}$, which together with the negative entropy of activation clearly supports the operation of an associative mechanism. A recent study provided mechanistic information on reductive elimination from cationic platinum(IV) complexes to form carbon–carbon bonds, and this is treated later in the appropriate section.

During a study of substitution reactions of dimethylhalo-platinum(IV) complexes in acetone, an intramolecular isomerisation was detected in two cases.²²⁷ The complexes were *cis*-($CH_3/S(CH_3)_2$) arranged dimethylhalo-platinum(IV) species in which PPh_3 substitutes the $S(CH_3)_2$ group. The isomerisation was monitored at low temperatures by 1H and ^{31}P NMR spectroscopies and could be described as a very energetically demanding turnstile twist-type reorganisation of the molecule following a significant degree of dissociation of the ligand. The activation parameters were ΔH^\ddagger of about 100 kJ mol^{-1} , $\Delta S^\ddagger = +88 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta V^\ddagger = +15$ and $+20 \text{ cm}^3 \text{ mol}^{-1}$. A substantial increase in volume in forming the transition state was therefore indicated. In other cases *mer/fac* ratio dispositions introduced complexities.

ISOMERISATION REACTIONS

As part of a comprehensive project aiming to develop metal-based reagents for the functionalisation of fluorocarbons, an unusual η^2 -vinyl isomerisation process was uncovered.²²⁸ As little information was available on the nature of the isomerisation of the tungsten(II)-based species, a detailed kinetics study was conducted.²²⁹ The reaction under consideration is shown in Scheme 8.

The kinetics could be monitored by IR and UV/visible spectroscopies in toluene as solvent. In the absence of added ligand the loss of reactant was first order, with activation parameters, $\Delta H^\ddagger = 124 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = +48 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta V^\ddagger = +15.6 \text{ cm}^3 \text{ mol}^{-1}$ at 60°C . These parameters were interpreted as being in accord with a limiting dissociative mechanism. The dissociation of CO is rate determining, followed by rapid isomerisation and recombination of CO. The reaction was also



Scheme 8.

studied in the presence of ligands (CO or P(OMe)₃) serving to promote the rate of reaction. Carbon monoxide enhances the reaction rate which depends on p(CO). The enthalpy of activation is about 25 kJ mol⁻¹ lower than the non-promoted reaction value, suggesting formation of a transition state with less bond breaking and some bond formation. The volume of activation is a small positive value (+3.9 cm³ mol⁻¹) which implied an intramolecular process with volume changes in an interchange mechanism almost mutually cancelling. The near zero entropy of activation was consistent with this proposal. Thus the attack by CO and subsequent release of coordinated CO were seen as a concerted process. In the case of the P(OMe)₃-promoted reaction, carried out in toluene at temperatures at or about room temperature, the product contains the P(OMe)₃ ligand coordinated to W *trans* to the coordinated fluorine and with the inserted acetylene moiety *cis* to the fluorine. The reaction is first order in the tungsten complex concentration and showed saturation kinetics at high [P(OMe)₃], a fact together with other evidence that indicated formation of an adduct before a step involving loss of CO. The activation parameters were obtained at both low and high ligand concentrations. This permitted extraction of both the volume change for formation of the precursor complex (+10 cm³ mol⁻¹) and that for the rate-determining step (+5.5 cm³ mol⁻¹). The former value was interpreted as arising from major rearrangement of the complex upon binding of P(OMe)₃, partially reflecting possibly the actual isomerisation process, for instance involving an η² to η¹ slippage. It was also acknowledged that desolvation of the entering ligand could make a contribution to the volume increase. The small value of the volume of activation for the rate-determining step is typical of values for a dissociative interchange ligand substitution mechanism (I_d). Steric congestion around the metal atom as a consequence of more W–CO bond lengthening than W–P bond shortening as the rigid η³-[C,N,N'] imine chelate ligand and the 2-vinyl group rearranged upon forming the transition state was the explanatory argument.

REDOX REACTIONS

Cobalt complexes with 14-membered tetraazamacrocyclic ligands have been investigated and successfully employed as catalysts for electrochemical and photochemical reduction of CO₂ and H₂O.²³⁰ One such complex low-spin [Co(I)HMD]⁺ (HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (hexamethylcyclam)) reacts with CO₂ in H₂O and in CH₃CN to form the *N-rac*-[CoHMD(CO₂)]⁺ species which is sufficiently stable in dry CH₃CN and in a CO₂

atmosphere to study the equilibrium between a purple five-coordinate form at room temperature and a yellow six-coordinate form at low temperatures.²³¹



The equilibrium system, in acetonitrile, has been studied by a variety of spectroscopic techniques, and after analysis it was concluded that the product could be interpreted as a Co(III)-CO₂ carboxylate complex,²³² meaning that the bound CO₂ has been reduced by a two electron transfer by the [Co(I)HMD]⁺ species. An additional perspective on the nature of this equilibrium was sought by application of pressure upon it in a pill-box cell, with spectrophotometric monitoring.²³³ Previously, the entropy of reaction at 15 °C had been determined. It was about -110 J mol⁻¹ K⁻¹, in accord with a highly ordered and compact six-coordinate species.²³⁴ Therefore, a markedly negative reaction volume could be predicted and was found; it was -17.7 cm³ mol⁻¹ at the same temperature in CH₃CN. It was argued that this can be a result of both a volume reduction upon addition of a solvent molecule, but that a larger contribution arises from the volume collapse due to the intramolecular electron transfer process accompanied by a shortening of the Co-CO₂ bond length, and an increase in electrostriction. Bond length reduction had been observed earlier in XANES and EXFAS studies.²³¹ Knowledge of the temperature and pressure dependence of this equilibrium provides an opportunity that allows, through their variation, precise tuning of the electron density on the Co and CO₂ sites.

Determining the mechanism of self-exchange reactions of metallocenes is a considerable challenge.²³⁵ Clarity has been brought to this subject following an investigation of the reaction between [η^5 -C₅(CH₃)₅Fe⁺] (DmFc⁺) and [η^5 -C₅(CH₃)₅Fe] (DmFc⁰) in deuterated acetone, dichloromethane and acetonitrile.²³⁶ The counter-ions were either hexafluorophosphate or tetrafluoroborate. Values of the exchange rate constant, k_{ex} , were obtained from ¹H NMR spectroscopic measurements at ambient and elevated pressures. Only very marginal effects of ion pairing were encountered. Values of ΔV^\ddagger were distinctly negative: -8.5 to -8.9 cm³ mol⁻¹ in (CD₃)₂CO and -6.3 to -7.2 cm³ mol⁻¹ in CD₂Cl₂. Fully quantitative results for the self-exchange in CD₃CN were precluded owing to practical limitations. The small variations in values of the volumes of activation arise when different concentrations or counter-ions are used. The self-exchange reaction at elevated pressures was modelled through an extension of Marcus-Hush theory. Various contributions to ΔV^\ddagger were carefully examined particularly with appropriate reference to non-aqueous solvents. It was concluded that the results were entirely consistent with a two-sphere activation model and it was not necessary to invoke solvent dynamics in the explanation. This high pressure study enabled counter arguments to be made against the proposal that solvent dynamics are involved in this type of electron self-exchange.²³⁷

In a related study, the volume of reaction, the volume of activation for diffusion ($\Delta V_{\text{diff}}^\ddagger$), and the volume of activation obtained from the standard electrode reaction rate constant at various pressures, have been determined for the decamethylferrocene (DmFc^{+ / 0}) system, in several non-aqueous solvents.²³⁸ The decamethylated ferrocene couple, rather than the unmethylated couple, was chosen. This

was because the large size of the former and low charge of the positive ion offer minimisation of complicating Coulombic interactions, such as ion-pairing. The unmethylated couple ($\text{Fc}^{+/0}$) is also less stable in the rigour of the electrochemical experimental conditions required. A further objective planned was a comparison of the pressure effects on the corresponding outer-sphere bimolecular electron transfer (self-exchange) rate constants in homogeneous solution with those on the non-aqueous electrode kinetics. The reaction volumes, ΔV_{cell} could be expressed as a linear function of the term Φ (the Drude–Nernst relation, $\Phi = (1/\epsilon) (\delta \ln \epsilon / \delta P)_T$ where ϵ is the solvent dielectric constant). $\Delta V_{\text{diff}}^\ddagger$ ranged from +7 to +17 $\text{cm}^3 \text{mol}^{-1}$ for the $\text{DmFc}^{+/0}$ system and generally increased with solvent viscosity. The values of $\Delta V_{\text{el}}^\ddagger$ for the electrode reaction of $\text{DmFc}^{+/0}$ were positive and within experimental uncertainty correspond to the relevant values of $\Delta V_{\text{diff}}^\ddagger$; this is in distinct contrast to the negative $\Delta V_{\text{exp}}^\ddagger$ values for the electron self-exchange in homogeneous solution. It was concluded that the electrode reactions were subject to solvent dynamical control. There was not a satisfactory relationship between the radii of the electro-active species obtained from the Drude–Nernst and Stokes–Einstein equations and radii related to crystallographic data; this discrepancy was discussed.

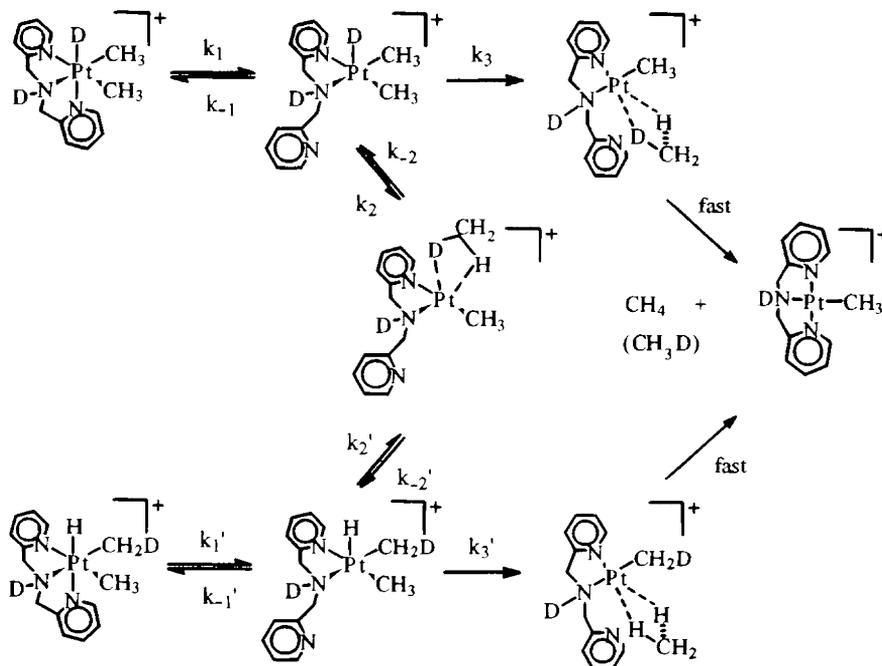
OXIDATIVE ADDITION AND REDUCTIVE ELIMINATION REACTIONS

Study of the catalytic oxidation of methane to methanol has witnessed a widespread use of Pt(II)/Pt(IV) complexes. A general scheme formulated on the basis of work by several investigators provided a level of understanding pertinent to about a decade ago.^{239–243} It was as follows. A labile Pt(II) species bonds methane to give an η^2 -methane complex which can interconvert to a five-coordinate methyl(hydrido)platinum(IV) complex. An additional ligand is required to stabilise the system. The additional ligand can be chloride or a nitrogen donor. Since both methane reductive elimination and methane activation pass through the same transition state the rationale was set for a study of methane elimination from a methyl(hydrido)platinum(IV) complex. The relevance for the mechanism of methane activation could then be accessed. Methane elimination from $[\text{Pt}(\text{H})(\text{CH}_3)(\text{BPMA})]^+$ where BPMA = bis(pyridylmethyl)amine could be monitored by NMR spectroscopic methods both at ambient and elevated pressures.²⁴⁴ By judicious use of acid (HBF_4OEt_2 or $\text{F}_3\text{CSO}_3\text{H}$) at a particular concentration level, it was possible to obtain kinetic data for both the *cis* and *trans* isomeric forms where the position of the hydride relative to the amine nitrogen determines the isomer. Solvents employed were deuterated forms of methylene dichloride or acetone. The *trans* isomer eliminates methane by a factor of 20 slower than the *cis* isomer. Respective volume of activation values were +6 (*cis*) and +8 $\text{cm}^3 \text{mol}^{-1}$ (*trans*), values that were lower than anticipated based on earlier reports. These values could be accounted for given that the rate law from which these parameters were obtained was a composite one in which a five-coordinate complex was treated as a steady-state intermediate. This conclusion for the *cis* isomer was also based on elaboration of the mechanistic treatment by studying the rate and stereochemistry of deuterium incorporation into

one methyl group. The findings could be summarised in a reaction scheme illustrating the unimolecular reaction of the *cis* isomer and its deuterated analogue to form a five-coordinate Pt complex by ring opening of a pyridyl moiety (Scheme 9).

In the *trans* isomer the pyridyl residue is *trans* to the weaker σ -donor methyl rather than the hydride in the *cis* isomer accounting for the slower reacting *trans* isomer. Following the formation of the five-coordinate intermediate, two reaction paths were possible: formation of η^2 -methane *cis* to the amine occupying position that then leads to elimination or formation of η^2 -bound methane *trans* to the amine site that leads to deuterium/proton scrambling. Following the generation of this reaction coordinate diagram, implications for methane activation can be judged by viewing the diagram in the reverse direction. One conclusion is that the highest energy of activation is required for substitution of a strong donor ligand by methane. Subsequently, interconversion into the five-coordinate methyl(hydrido)platinum(IV) complex and ring closure to yield a stable six-coordinate complex are very facile processes.

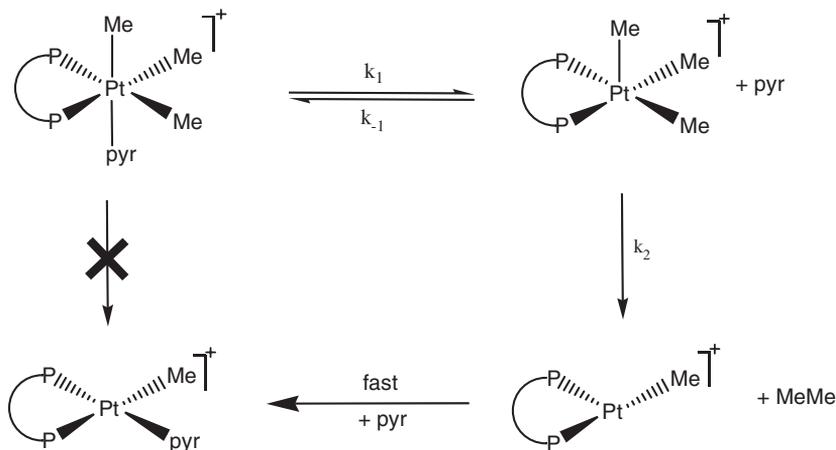
A very recent report moves forward significantly understanding the mechanism of reductive elimination reactions to form carbon-carbon bonds from platinum(IV) complexes.²⁴⁵ This report described the kinetics of reductive elimination from a cationic platinum(IV) complex as a function of solvent, of substituent character in a leaving group, of the potential effect of different spectator ligands and addressed whether there was a kinetic isotope effect. The reactions were studied also as a



Scheme 9.

function of temperature and of hydrostatic pressure. Earlier neutral platinum(IV) complexes of the type *fac*-[(L₂)PtMe₃X], X = halide, carboxylate, aryloxy; L = a monodentate phosphine (PMe₂Ph, PMePh₂) or L₂ = a bidentate diphosphine (dppe = bis(diphenylphosphino)ethane, dppbz = *o*-bis(diphenylphosphino)benzene) were shown to undergo reductive elimination to form carbon–carbon and/or carbon–heteroatom bonds.^{246–249} Kinetic studies on these complexes showed that for C–C and C–X reductive elimination reactions investigated, dissociation of a ligand occurred prior to the actual reductive coupling. The exact nature of the six-coordinate state to five-coordinate intermediate conversion depended on L, L₂ and X, but a five-coordinate intermediate could always be proposed if not based on actual, but on circumstantial evidence. Since electron withdrawing groups in X, addition of Lewis acids and solvent polarity changes all had influence upon the kinetic parameters, it was clear that variations among these reaction conditions could influence the extent of, or select for C–C or C–X coupling. Against this background and with a desire to form exclusively C–C coupled products, reductive elimination kinetic studies from cationic species *fac*-{[(L₂)Pt(IV)Me₃(pyr-X)][Otf]}⁺, L₂ = dppe and dppbz, with pyr = pyridine and four-substituted derivatives NC₅H₄X (pyr-X) were undertaken.²⁴⁵ Pre-equilibrium dissociation of the pyridine ligand from the Pt(IV) complex was shown to be responsible for the inverse dependence of the observed rate constant on the concentration of added pyridine. This implied that reductive elimination occurred from a five-coordinate cationic intermediate or from a six-coordinate solvento complex containing a weakly bound solvent molecule. The reaction rates were independent of solvent over a broad range of dielectric constant, compelling evidence for absence of a solvento six-coordinate intermediate and reinforced the view that elimination was from a cationic five-coordinate species. The dppe complex reacted about 3.5 times faster than the complex containing the dppbz spectator ligand, a moderate effect. The dppbz complex could bring about lower electron density on the MC, a property that may affect either or both of the reaction steps. A kinetic isotope of 1.1 for reaction of the deuterated pyr-d⁵ complex was also consistent with the proposed mechanism of pyridine dissociation followed by carbon–carbon coupling (Scheme 10).

A linear free energy correlation based on four-substituted pyridine substituent constants yielded a value of ρ of 1.9; the reaction is considerably faster for more electron withdrawing substituents, i.e. better leaving groups. The proposed mechanism would signify that the value applies only to the first reaction step since the second does not involve pyridine(s). While cognisant of the difficulty of using substituent constants based on ionisation properties, nevertheless the value of ρ could be rationalised as reasonable. Activation parameters of 160 kJ mol⁻¹, +180 J mol⁻¹ K⁻¹ and +16 cm³ mol⁻¹ for ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger were obtained, respectively. From the two-step mechanistic scheme and the derived rate law, subject to certain conditions, these parameters represent the change in the given property for the equilibrium relating to the first step of pyridine departure plus that for reaching the transition state of the second step. The thermal activation parameters were consistent with those obtained for reductive elimination from platinum(IV) neutral complexes,²⁴⁶ and since more molecular disorder is occurring in both steps in reaction of the



Scheme 10.

cationic complexes the large positive entropy is compatible with those events. Considering precedents for volume of activation values and the partial molar volume of ethane ($52.4 \text{ cm}^3 \text{ mol}^{-1}$), the significantly positive volume of activation that was determined supports the mechanistic scheme.

REACTIONS OF SMALL MOLECULES

There have been many studies in which the kinetics of dioxygen and carbon monoxide binding to myoglobins, haemoglobins and to porphyrin-based model complexes,^{250–252} and also to some cobalt(II) complexes that bind dioxygen reversibly,²⁵³ have been investigated and in which in some cases the pressure dependence of the kinetic parameters has been established. Iron(II) cyclidene compounds are non-porphyrin complexes that have been employed as functional mimics for binding of these small molecules.²⁵⁴ The kinetics of the forward and reverse reactions of CO binding to the iron(II) cyclidene complex, $\text{Fe}(\text{II})(\text{PhBzXy})(\text{PF}_6)_2$, have been monitored as a function of temperature and pressure in acetonitrile and an illustrative volume profile developed (Fig. 16).^{255,256}

The complex $\text{Fe}(\text{II})(\text{PhBzXy})(\text{PF}_6)_2$ exists in solution as a five-coordinate species, $(\text{B})\text{Fe}(\text{II})\text{L}$, in which L is the macrocycle supplying four equatorial nitrogen donors and the fifth outside axial position is occupied by a coordinated solvent molecule (acetonitrile). Coordination of a sixth ligand, for example CO, was characterised as a bimolecular process, in the presence of a base molecule.²⁵⁷



The reaction volume could be obtained from the pressure dependence of the equilibrium constant as $-47.7 \text{ cm}^3 \text{ mol}^{-1}$, in excellent agreement with the value obtained from the kinetically determined value of $-48.3 \text{ cm}^3 \text{ mol}^{-1}$ (reaction

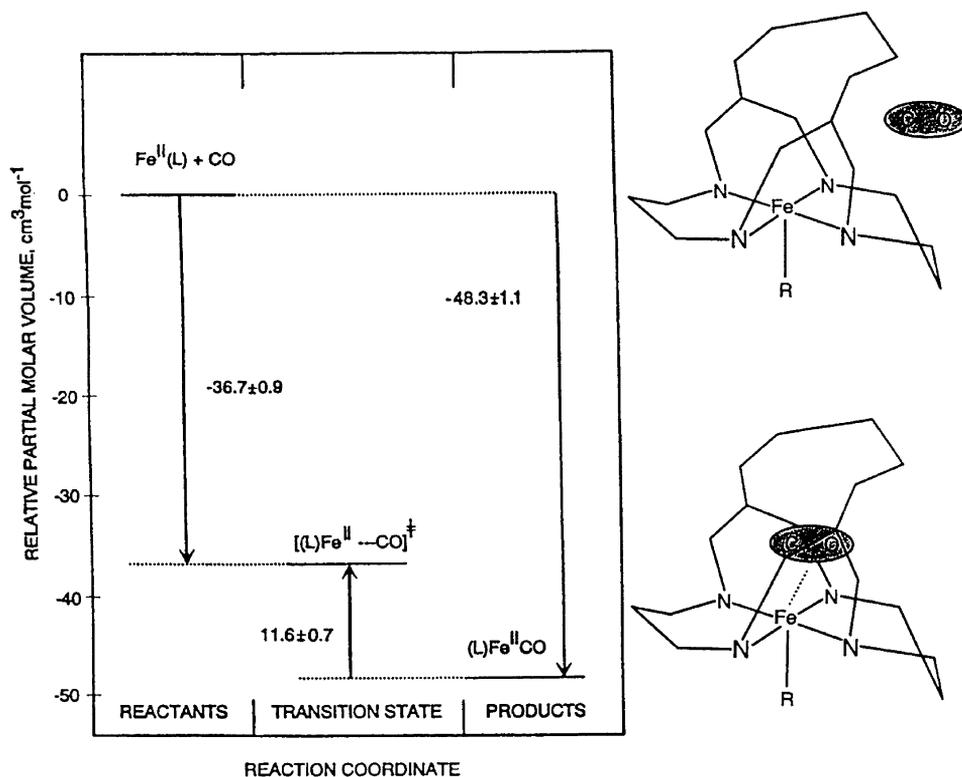


Fig. 16 Volume profile for the reversible binding of CO to a lacunar Fe(II) complex.

volume = $\Delta V_{\text{on}}^{\ddagger}$ ($-36.9 \text{ cm}^3 \text{ mol}^{-1}$) - $\Delta V_{\text{off}}^{\ddagger}$ ($+11.6 \text{ cm}^3 \text{ mol}^{-1}$). The markedly negative value for the forward (on) reaction was taken to signify that CO is virtually enveloped within the structure of the iron complex. Indeed the reduction in volume is close to that of the partial molar volume of CO (33 and $44 \text{ cm}^3 \text{ mol}^{-1}$ in aqueous solution and 1,2-dichloroethane, respectively).^{258,259} There is a spin change upon binding of CO from the high-spin five-coordinate species to the low-spin six-coordinate species. This factor was also considered in interpreting the activation volume as well as the fact that the iron that is out of the plane of the equatorial ligands in the former coordinate state but moves towards the plane upon forming a six-coordinate state. It was proposed that the spin change occurs after the transition state is reached in the forward direction meaning that the volume increase that occurred upon reaching the transition state in the reverse direction is attributable to the spin state change and also to the movement of iron(II) out of the ligand plane as partial bond breakage Fe-CO begins. Thus the transition state was envisaged as a high-spin iron(II)-CO species, late in the forward direction and early in the reverse direction. The large negative entropy of activation in the forward direction ($-108 \text{ J mol}^{-1} \text{ K}^{-1}$) corresponded to the loss of degrees of freedom of CO. Weakening of the iron-CO bond and the spin state change accounted for the positive entropy of activation

(+ 30 J mol⁻¹ K⁻¹) in the reverse direction. Free energy, entropy as well as volume profiles were presented. The thermodynamic parameters were similar to those found for binding of CO to myoglobin.

ADDITION REACTIONS

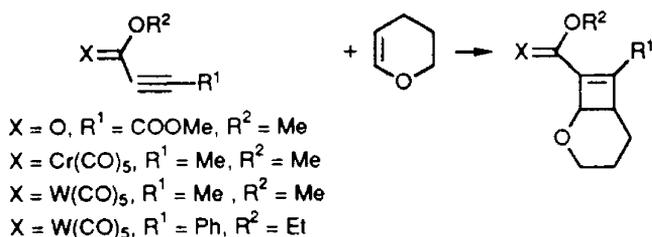
Cycloaddition reactions of derivatives of chromium and tungsten pentacarbonyl compounds

Addition reactions can be expected, in principle, to involve significant bond formation in the transition state, such that reaction acceleration would be anticipated at elevated pressures. Reactions of the type illustrated in Scheme 11, [2 + 2] cycloadditions, were significantly accelerated by pressure and there was almost no dependence on the polarity of the solvent.²⁶⁰

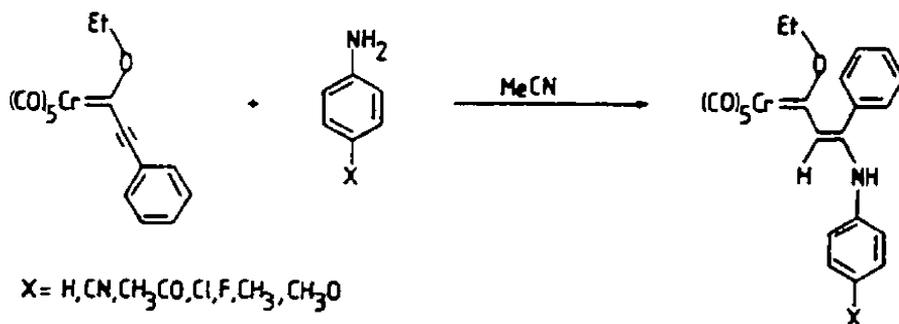
An average value of ΔV^\ddagger was $-16 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$. This together with the reaction rates being independent of solvent suggested the reaction followed a non-polar concerted synchronous one-step mechanism. The insertion of dipropylcyanamide and 1-(diethylamino)propene into the metal-carbene bond of pentacarbonyl(methoxyphenylcarbene)chromium and tungsten had earlier been found also to yield significantly negative volumes of activation (-17 to $-25 \text{ cm}^3 \text{ mol}^{-1}$).²⁶¹

Addition reactions of metal pentacarbonyl α , β -unsaturated Fischer carbene complexes

In acetonitrile all reactions of pyrrolidine addition exhibited ΔV^\ddagger values between -15 and $-17 \text{ cm}^3 \text{ mol}^{-1}$.²⁶² However, upon decreasing the solvent polarity, ΔV^\ddagger became markedly more negative and a good correlation with the solvent parameter q_p (i.e. the pressure derivative of q , the polarisability of the solvent) could be demonstrated. It was concluded that the addition of pyrrolidine followed a two-step process with a polar transition state leading to a zwitterionic intermediate. Addition of *para*-substituted anilines to a similar Fischer carbene complex in acetonitrile was characterised by more negative values of ΔV^\ddagger (-21 to $-27 \text{ cm}^3 \text{ mol}^{-1}$) than those for addition of pyrrolidine.²⁶³ Second-order rate constants for the addition reaction exhibited an excellent correlation with the basicity of the aniline derivatives used. The trend in activation volumes could be correlated with an early or late transition state for the fast and slow addition reactions, respectively Scheme 12.



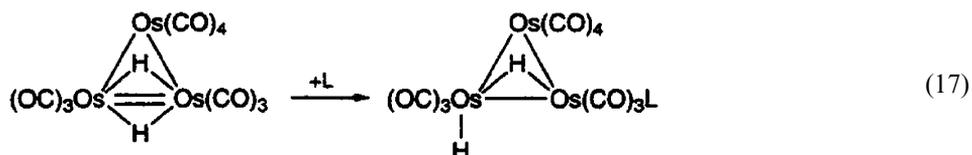
Scheme 11.



Scheme 12.

Addition to an osmium cluster

The unsaturated osmium hydrido carbonyl cluster $(\mu_2\text{-H})_2\text{Os}_3(\text{CO})_{10}$ reacts with a wide variety of Lewis bases, L,²⁶⁴ according to the following equation:



The addition of several P-donor ligands to the cluster in non-polar solvents was monitored spectrophotometrically. From the kinetics results clear, quantitative, electronic and steric profiles for the associative reaction based on the electronic and steric properties of the nucleophiles were provided.²⁶⁵ The second-order rate constants could be correlated with the $\text{p}K_{\text{a}}$ values of the ligands. The $\text{p}K_{\text{a}}$ value is a property related to its σ -donicity. This aspect addresses the electronic effect of the added nucleophile. Potential steric effects upon the rate constant were addressed by considering both the cone angle and size of the nucleophile. An equation combining these principles was developed and with various parameters was able to correlate both electronic and steric effects. It was also pointed out that when the cone angle is lower than a critical threshold value, in the transition state the cluster provided a well-defined open space in the coordination sphere offering negligible repulsion to small entering donors. Notwithstanding this successful description of the reaction, a further comprehensive investigation of the reaction was undertaken in which 18 P-donor nucleophiles were employed.²⁶⁶ The objective was to acquire the thermal- and pressure-derived activation parameters and determine whether similar correlations could be developed that could provide a further classification of the transition state, and indeed a novel and detailed picture of the transition state nature. The second-order rate constants for reactions in chlorobenzene, determined spectrophotometrically, followed the same empirical equation that had been developed for reactions in heptane. A term for the σ -donicity of the nucleophiles in non-polar solvents was applied for ligand electronic effects. Steric effects were not observed for ligands with a Tolman cone angle below the steric threshold of 147° . Larger ligands

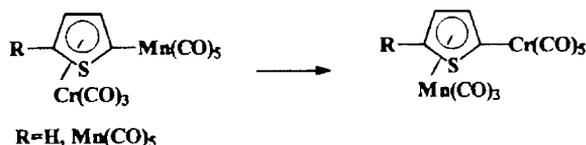
have a significant effect upon the rate constant. Reaction of PPh_3 with the osmium cluster was characterised by a similar rate constant in heptane and nitrobenzene, but a slightly lower value when the solvent was chlorobenzene. These findings were taken to imply that the transition state for a given nucleophile remains essentially unchanged in different solvents. In all cases the entropies and volumes of activation were distinctly negative, the former typically in the range of -90 to $-170 \text{ J mol}^{-1} \text{ K}^{-1}$, and the latter almost all in the range of -12 to $-26 \text{ cm}^3 \text{ mol}^{-1}$. A plot of ΔH^\ddagger versus ΔS^\ddagger could be interpreted to indicate the reaction rates are largely entropy controlled. The large negative values of ΔV^\ddagger (obtained in chlorobenzene) for the associative process are in accord with values for other associative reactions such as Michael addition, insertion reactions and $[2+2]$ -cycloadditions. Values for isosteric ligands were invariant and since there was no dependence on σ -donicity, the volume reduction upon forming the transition state depended only on steric factors and not on nucleophile basicity. A geometrical model was developed based on the ligand cone angle and an equation formulated that could account for the observed volume of activation in terms of an intrinsic component and a volume term based on the volume of a ligand based on its cone angle. In fact this treatment is one of the most detailed analysis of volumes of activation in organometallic kinetics literature. The correlation of ΔV^\ddagger values with ligand cone angles was described as remarkable. For cone angles less than 160° , ΔV^\ddagger decreases linearly with a term that is a measure of the relative volume of the nucleophile. This suggested that the $\text{Os}\cdots\text{P}$ bond lengths in the transition state are the same for these nucleophiles, and enabled an estimate to be made of the penetration (ca. 24 pm) of the P-donor ligands inside the periphery of the cluster in the transition state. When the cone angle is 160° a new type of steric threshold appeared and above this value the volumes of activation become less negative, ligand penetration is lower and $\text{Os}\cdots\text{P}$ bond lengths become progressively longer. Practical limitations prevented determination of volume profiles. It is possible that these would have revealed evidence for early or late transition states. Nevertheless this report represents a landmark of thorough and valuable analysis and insight into the reaction mechanism.

OTHER REACTIONS

Metal exchange in heterobimetallic compounds

Interest in the coordination chemistry of thiophene and in model studies of the absorption process involved in hydrodesulfurisation in the petroleum industry led to the development of bimetallic and trimetallic complexes containing thiophene.²⁶⁷ Of greater interest was the finding of irreversible exchange (σ and π) of coordination sites by metal fragments. An example of the reaction is shown in [Scheme 13](#).

This finding was followed by a comprehensive preparative, structural characterisation and kinetics study of the conversions typified by the reaction above.²⁶⁸ These reactions were accorded the term metal exchange reactions. The heterobimetallic complexes with σ , π bridging thiophene or selenophene ligands ($\eta^1:\eta^5$ - $\text{XCRCHCHCM}_n(\text{CO})_5\text{Cr}(\text{CO})_3$ ($\text{X} = \text{S}$, $\text{R} = \text{H}$ (**1**); $\text{R} = \text{Me}$ (**2**); $\text{X} = \text{Se}$, $\text{R} = \text{H}$



Scheme 13.

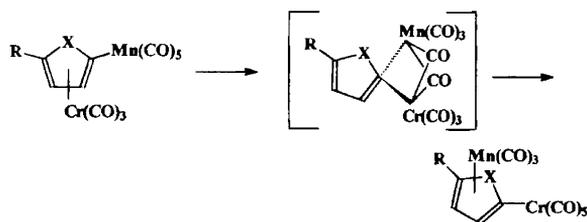
(3) converted irreversibly at 0 °C in acetone into the complexes ($\eta^1:\eta^5$ -XCRCHCHCCr(CO)₃Mn(CO)₃) ((4), (5) and (6)), respectively. Changes in the UV/visible, IR and NMR spectra accompany these transformations. The kinetics of the reaction of (2)–(5) were monitored by UV/visible spectrophotometry; the first-order rate constant was essentially independent of the concentration of (2), and not significantly affected by variation of solvent employed. Solvents ranged from cyclohexane ($\epsilon = 2.02$), tetrahydrofuran ($\epsilon = 7.3$), dichloromethane ($\epsilon = 8.9$) to acetone ($\epsilon = 21$), and the rate constants were, respectively 11, 36, 26 and 38, all $\times 10^6 \text{ s}^{-1}$ at 15 °C. Comparable rate constants were determined for the reaction of (2)–(5) in *d*₆-acetone or *d*₂-dichloromethane by ¹H NMR spectroscopy, and no intermediates were observed. These findings indicated that solvent polarity does not play an important role in the metal exchange reaction and therefore direct participation of coordinated solvent molecules in the transition state could be ruled out. Thermal activation parameters were established for the conversions of compounds (1) and (2) and were 93 and 86 kJ mol⁻¹ (enthalpies) and -16 ± 6 and $-30 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$ (entropies), respectively. The former are values associated with covalent bond cleavage, while the latter are modest values and were considered to point to an intramolecular exchange process. A near zero ($-0.6 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$) volume of activation for the conversion of (2)–(5) substantiated this conclusion and excluded the possibility of an intermolecular arene displacement route. A scheme invoking bridging carbonyl ligands in which the MCs were η^1 -bonded to the C2 of the thienyl ligand with the two bridging carbonyls occupying the free coordination sites was proposed. It could also be concluded that there were no measurable changes in electrostriction upon reaching the transition state (Scheme 14).

It was also noted that of the metal exchange reactions investigated the thermodynamically favoured product was always less polar than the starting material.

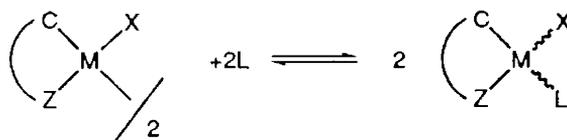
Monomerisation of dinuclear pallada- and platina-cycles

A complementary structural and kinetics characterisation study regarding the halogen cleavage reaction (by pyridines) in dimethylaminomethylphenyl-C¹,N pallada- and platina-cycles has been reported (see Scheme 15).²⁶⁹ This work followed by 30 years a pioneering study of the kinetics of monomerisation of a dinuclear bromine-bridged platinum compound using pyridine.²⁷⁰

Reactions of this type are postulated as equilibria in synthetically important insertion reactions of alkenes, alkynes and other unsaturated molecules into the Pd–C bonds of dimeric palladacycles.^{271,272} Further, this reaction can form the basis for



Scheme 14.



Scheme 15 M = Pd(II) and Pt(II), X = halogen bridge, Z = N, P, S, etc., and L = donor ligand.

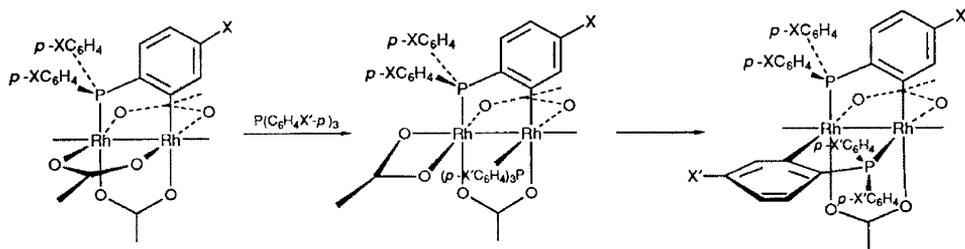
synthesis of monomeric metallacycles from the corresponding dimers.²⁷³ Specifically, the halogen-bridge cleavage reaction of $[\{M(o-C_6H_3RCH_2NMe_2)X\}_2]$ (M = Pd or Pt; R = H, 4-MeO, 5-Me, or 5-F; X = Cl or I) by a series of substituted pyridines in chloroform has been investigated as a function of concentration of excess pyridine, of temperature and when experimentally feasible as a function of hydrostatic pressure. The reactions were rapid and of second order, and showed strong steric rather than electronic demands, and there was no evidence of a reverse reaction confirming the essential irreversibility. Five dimeric Pd compounds reacted with essentially the same rates and thermal activation parameters with pyridine; the five included widely varying electron/donating/withdrawing groups (R) and change of Cl by I. This led to the conclusion that reaction rates demonstrated electronic insensitivity. However, varying the steric features of the pyridine nucleophiles (4-Me, 2,4-Me₂ and 2,6-Me₂) had a significant retarding effect, in that order. Steric hindrance in the vicinity of the donor centre was indicative of an associative mechanism. Further evidence for the associative nature of the bridge-cleavage reaction came from interpretation of the activation parameters. The enthalpies of activation were regarded as lower than would be compatible with incipient bond breakage as the transition state is formed in a dissociative mechanism. The ΔS^\ddagger values, in the range of -104 to $-158 \text{ J mol}^{-1} \text{ K}^{-1}$, suggested the transition state is highly ordered, and included back donation from the metal into the apically coordinated pyridine ligand. In two cases the rates of monomerisation could be studied as a function of pressure. The compound with M = Pd, R = H and X = I upon reaction with 2,6-diMe₂py converted to the monomeric form with $\Delta V^\ddagger = -22.6 \text{ cm}^3 \text{ mol}^{-1}$, whereas the platinum compound with R = 4-MeO and X = Cl, upon reaction with 4-Mepy yielded ΔV^\ddagger of $-14.5 \text{ cm}^3 \text{ mol}^{-1}$. These distinctly negative values remove any doubt; these reactions are emphatically associative. The smaller volume change for the platinum compound reaction was thought to reflect partly the smaller entering group. Thus, a comprehensive kinetics study in which the

activation parameters were obtained has illuminated the reaction mechanism of a type of system first studied decades earlier.

Cyclometallation in dirhodium(II) compounds

Cyclometallation reactions of mononuclear compounds are well established,²⁷⁴ but such reactions occurring on compounds having two MCs are not as well known. To address the lack of information regarding the mechanism of the latter reactions a systematic study of the reactivity of arylphosphines in dirhodium(II) compounds that give rise to cyclometallation was undertaken.²⁷⁵ The compounds were $[\text{Rh}_2(\text{O}_2\text{CMe})(\mu\text{-O}_2\text{CMe})_2\{\mu\text{-(XC}_6\text{H}_3\text{)P(C}_6\text{H}_4\text{X-p)}_2\}\{\text{P(C}_6\text{H}_4\text{X'-p)}_3\}]$ ($\text{X} = \text{H}$, $\text{X}' = \text{H}$ or Me ; $\text{X} = \text{Me}$, $\text{X}' = \text{H}$ or Me) and they underwent reaction to produce the corresponding doubly metallated compounds $[\text{Rh}_2(\mu\text{-O}_2\text{CMe})_2\{\mu\text{-(XC}_6\text{H}_3\text{)P(C}_6\text{H}_4\text{X-p)}_2\}_2]$. The reactant possessed a metallated and an equatorial phosphine in a head-to-tail cisoid configuration (see Scheme 16).

The kinetics of the reaction have been studied under a multitude of variables and conditions, including toluene and glacial acetic acid as solvent, thermal, acid- and base-assisted conditions, different bases (PPh_3 , $\text{P(C}_6\text{H}_4\text{Me-p)}_3$ or pyridine), and as a function of temperature, pressure and base concentration. Depending on the conditions, reaction paths differed such that a substitution path as well as metallation was revealed. The doubly metallated compounds were shown by ^{31}P NMR spectroscopy to retain the head-to-tail cisoid configuration. Activation parameters were acquired for several permutations of reactant variation and base variations for the spontaneous, acid- and base-assisted reactions. All values of the volume of activation were significantly negative: they were in the range of -23 to $-37\text{ cm}^3\text{ mol}^{-1}$, -21 to $-23\text{ cm}^3\text{ mol}^{-1}$ and -14 or $-15\text{ cm}^3\text{ mol}^{-1}$, for the base-assisted, spontaneous and acid-assisted processes, respectively. This indicated that compression of the system as the transition state is reached is clearly important. The less negative values for the base-assisted reaction were observed when the base was pyridine. This was proposed to relate to smaller steric demands compared with the values when the base in question was PPh_3 . Presumably owing to the complexity of the system, no detailed breakdown of contributions to the volumes of activation was offered. The entropies of activation mirrored the latter, supporting a measure of ordering in the transition state. The absence of electrostriction changes in forming the transition state could be inferred.

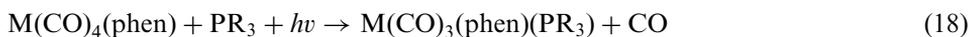


Scheme 16 Axial positions are occupied by any Lewis base present in solution. X , $\text{X}' = \text{H}$ or Me .

4 Volumes of activation for radiation-induced organometallic reactions

PHOTO-INDUCED REACTIONS

The photochemically induced substitution of one or more CO ligands in $M(\text{CO})_4(\text{diimine})$, ($M = \text{Cr}, \text{Mo}, \text{W}$ and diimine = phen or bpy) by an incoming nucleophile has been investigated with the purpose of understanding the reaction mechanism, over a considerable time period.²⁷⁶ Using PEt_3 as the entering nucleophile it was shown that the mechanism of substitution on $M(\text{CO})_4(\text{phen})$ in toluene could vary depending on whether excitation occurred through a low energy metal-to-ligand charge transfer (MLCT) band or via a ligand field (LF) wavelength.^{277–279} In the latter case on the basis of analysis of quantum yields and the pressure dependence of the kinetics of the substitution the mechanism was assigned as dissociative. For substitution following MLCT excitation a mechanistic change-over to an associative one, when $M = \text{Mo}, \text{W}$, was proposed on the basis of results analysis. The changeover was explained by proposing that upon MLCT excitation electron density is transferred away from the MC onto the phen ligand, enabling an associative attack by the entering nucleophile at the more electrophilic MC. Whereas following LF excitation a lengthening of the metal–ligand bond occurs, promoting dissociative ligand substitution. When $M = \text{Cr}$ the pressure dependence of the reaction progress indicated a less marked variation, a change from a D to an I_d mechanism. This finding could be rationalised on the basis of a smaller Cr centre, relatively to Mo and W, influencing the extent of bond formation in the MLCT excited state. A series of further pivotal studies in which nucleophiles and their respective concentrations, the irradiation wavelengths and hydrostatic pressure were all varied, was reported.^{280–282} A systematic tuning of the photo-substitution mechanism was discerned by changes in the physical and chemical variables. A first report addressed the issue of how the mechanism might be affected by nucleophile bulk by using PMe_3 and PPh_3 as entering nucleophiles for photo-substitution on the chromium compound. The overall reaction is given in the following equation:



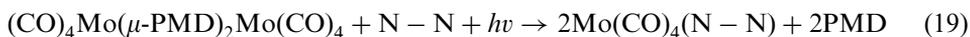
A complete reaction scheme was presented based on the accumulated results including a possible step in which a solvent molecule is temporarily attached to the compound. LF photolysis is decelerated markedly upon pressure increase, consistent with a limiting D mechanism. Ligand substitution proceeds by a dissociative interchange mechanism following MLCT photolysis, and results for the two entering nucleophiles were rather similar demonstrating that relatively little bond formation occurs with the entering nucleophile. A second report describes a corresponding study upon the molybdenum and tungsten analogues. From the measurement of the pressure dependence of the quantum yield apparent volumes of activation could be determined at each irradiating wavelength, and could be analysed in terms of contributions arising from dissociative LF excitation and associative MLCT excitation.

Steric crowding caused by the PPh_3 nucleophile can hinder an associative ligand substitution process. Together these results for the different metals and different entering nucleophiles, including additional results for reaction when $\text{R} = \text{Bu}^n$ were assessed and a scheme was presented that included the three possible pathways via D, I or A mechanisms for nucleophilic substitution from the excited state species $[\text{M}(\text{CO})_4(\text{phen})]^*$. A clear example of a mechanistic changeover was presented for the reaction of PBU_3^n with $[\text{W}(\text{CO})_4(\text{phen})]$ for which the volume of activation for the quantum yield ranged from $+10.5$ to $-12.0 \text{ cm}^3 \text{ mol}^{-1}$ as the wavelength varied from 313 to 546 nm. A pattern of systematic variation in the mechanism of substitution could be extracted from results obtained by variation of the metal, entering nucleophile, nucleophile concentration, excitation wavelength and applied pressure. While analysis of ambient pressure results is fruitful, the key distinguishing feature regarding mechanism is the pressure dependence leading to the volume of activation.

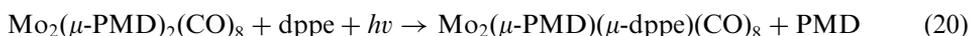
The mechanism of reactions in which photolysis of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in the presence of a bidentate ligand in toluene leads to first a pentacarbonyl intermediate, followed by a mono-coordinated bidentate ligand and subsequent chelate ring closure with expulsion of a second CO ligand was thought to be understood.²⁸³ That is for bidentate ligands phen, en and dab (en, dab = 1,4-diisopropyl-1,4-diazabutadiene), the volume of activation for the ring-closure step was significantly negative supporting the operation of an associatively activated chelation mechanism for $\text{M} = \text{Mo}$ and W . When $\text{M} = \text{Cr}$ the volume of activation value suggested a fine balance between the size of the MC and steric hindrance on the free end of the bidentate ligand as the transition state was approached. Hence for chromium complexes the chelation mechanism could proceed by an associative or dissociative mechanism. Subsequently it was shown that under certain conditions chromium binuclear bridged species and $\text{Cr}(\text{CO})_5(\text{dab})$ could be isolated, raising concerns that other species may have (unknowingly) been present in the earlier ring-closure studies.²⁸⁴ Accordingly, thermal ring-closure reactions of pentacarbonylchromium complexes with bidentate ligands dab (in *n*-heptane) and dmbpy (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) (in toluene) were studied thoroughly. This was made possible by first isolating some of the monodentate pentacarbonyl chromium complexes. The kinetics were studied as a function of N–N (= dab or dmbpy) concentration, temperature and pressure.²⁸³ The finding of a decrease in observed rate constant with increasing N–N concentration was interpreted in terms of competing reactions leading to the formation of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_4(\text{N–N})$. At high N–N the limiting rate constant represents only the chelation reaction for which activation volumes could be determined. These ranged from $+13$ to $+18 \text{ cm}^3 \text{ mol}^{-1}$ and strongly support the operation of a dissociatively activated chelation mechanism.

Since the molybdenum compounds described above demonstrated mechanistic variation in photochemically initiated substitution reactions, the molybdenum dimetallacycle $[(\text{CO})_4\text{Mo}(\mu\text{-PMD})_2\text{Mo}(\text{CO})_4]$ was selected for a study of the nature of the substitution mechanism associated with MC and MLCT excitation.²⁸⁵ PMD is pentamethylenediazirine. The substituting ligands were bpy, phen and 1,2-bis(diphenylphosphino)ethane (dppe) for the reaction in toluene solution. For reaction with

bpy and phen (N–N) the irradiation leads to cleavage of the metal–diazirine bonds according to the following equation:



Analysis of the results obtained by studying this reaction as a function of ligand concentration and pressure indicated that the photochemical reaction is in competition with a thermal reaction. For MC photolysis the photochemical reaction proceeds by a dissociative (D) route whereas the thermal reaction proceeds according to an associative (A) mechanism. This conclusion was reached primarily on the basis of the sign and magnitude of the volumes of activation extracted from the kinetic data. The reaction with dppe proceeds by displacing one bridging PMD ligand (Equation (20)), or by releasing CO to generate $\text{Mo}_2(\mu\text{-PMD})_2(\mu\text{-dppe})(\text{CO})_6$:



Experimental results following MLCT excitation yielded significantly negative volumes of activation, indicating associative substitution mechanisms for both the MLCT initiated and thermal substitution processes. The concentration dependencies and magnitude of the activation volumes yielded no evidence for an interchange mechanism. A complete scheme indicating the photochemical, thermal, rate determining and rapid reaction steps was assembled.

Photo-induced homolysis reactions have been observed for a wide variety of metal–metal bonded complexes containing an α -diimine moiety.^{286,287} The subsequent fate of the metal radicals has been investigated in detail for complexes such as $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{diimine})$.²⁸⁸ In non-coordinating, non-viscous solvents the radicals diffuse from the solvent cage and dimerise, whereas in coordinating solvents this complex photodisproportionates, in the presence of an N- or P-donor ligand (L), into $\text{Mn}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_3(\text{L})(\text{diimine})^+$. These interesting findings prompted a similar study on a metal triangular cluster, $\text{Os}_3(\text{CO})_{10}(\text{diimine})$.²⁸⁹ In acetonitrile and pyridine (S), zwitterions of the type $^-\text{Os}(\text{CO})_4\text{-Os}(\text{CO})_4\text{-Os}^+(\text{S})(\text{CO})_2(\text{diimine})$ were generated although the mechanism of formation was unclear. There was no evidence at this stage of biradical formation in any solvents investigated. A subsequent study established by electron paramagnetic resonance and nanosecond transient absorption spectroscopies, the formation of biradicals.²⁹⁰ Conversion of the biradical species to zwitterions was also monitored. In order to clarify the mechanism of zwitterion formation, the osmium cluster containing the diimine, 2-acetylpyridine *N-n*-propylimine, in pyridine was irradiated in a pill-box cell, high pressure cell arrangement in the pressure range up to 150 MPa. The pressure dependence of the quantum yield afforded an apparent activation volume of $+7.5 \text{ cm}^3 \text{ mol}^{-1}$, a value that might not have been anticipated in view of the marked increase in electrostriction accompanying zwitterion formation and lower intrinsic volume arising from solvent coordination. The result was explained by invoking bond cleavage, the positive volume change for which is partly offset by the increase of electrostriction and coordination of pyridine.

Catalytic schemes for carbon monoxide activation required for methanol carbonylation to acetic acid and alkene hydroformylation often depend on a carbon

monoxide insertion into a metal alkyl bond in a critical carbon–carbon bond formation step.²⁹¹ Progress in elucidating reactivities and structures of intermediates in such processes is beset with difficulties owing to low concentrations of relevant species. One approach has been to generate potentially pertinent intermediates by flash photolysis and examine the properties of transient species by time-resolved optical and TRIR spectroscopies.^{292,293} Reactions of the decarbonylated intermediate generated from the excited state of the photolysis of $\text{CpFe}(\text{CO})_2(\text{C}(\text{O})\text{CH}_3)$ in heptane have been studied in order to resolve the kinetic characteristics of a step in which the intermediate reacts with a ligand, rate constant, k_L , to yield $\text{CpFe}(\text{CO})(\text{C}(\text{O}))(\text{CH}_3)(\text{L}) = \text{A}_L$ and another step, rate constant, k_m , in which the species formed is $\text{CpFe}(\text{CO})_2(\text{CH}_3) = \text{M}$.²⁹⁴ Measurements applying hydrostatic pressure were carried out and these resulted in clarification of mechanistic proposals made earlier. A detailed analysis of the derivation of volumes of activation for these steps from quantum yield measurements was presented, and use of the method yielded $\Delta V_L^\ddagger - \Delta V_m^\ddagger = -5 \text{ cm}^3 \text{ mol}^{-1}$. A similar value was established for the parallel reactions of the compound in which Cp is replaced by the indenyl (Ind) moiety. These $\Delta\Delta V^\ddagger$ values suggest transition states that are not dramatically different in character for the two pathways for each of the respective Cp and Ind compounds. One possible explanation suggested was that both pathways are concerted reactions involving a solvento species and it was argued that k_m would be independent of pressure thus attributing the numerical value of the difference entirely to the pressure dependence of k_L . The improved experimental approach applying FTIR enabled a mechanism, previously advanced, based on ring slippage, to be ruled out.

PULSE-RADIOLYSIS-INDUCED REACTIONS

Transition metal–carbon σ -bonds can be key intermediates in industrial processes, biochemical reactions, organic synthesis and in catalytic processes. The pulse radiolysis method can generate from the primary species formed in aqueous medium, secondary species depending on the solutes present. Aliphatic radicals, for example, can then react with metal-aqua ions or metal complexes to form complexes with metal–carbon σ -bonds. The subsequent reactivity of these species or the products can then be monitored, usually spectrophotometrically. The radicals are generated in sub-microsecond times, and very rapid processes ensue, requiring specialised methods. As cited earlier, two authoritative reviews have been published recently,^{108,109} the former emphasising the application of high pressure methods in kinetics and mechanistic studies of species generated by pulse radiolysis. The second covers comprehensively the research conducted regarding kinetics and mechanistic studies over the past 30 years. This includes as well, accounts of the properties, spectra and acid dissociation constants, as appropriate, for complexes containing metal–carbon σ -bonds. A section on mechanistic features has 11 sub-sections, e.g. heterolysis and homolysis of metal–carbon σ -bonds, β -elimination reactions, CO insertion/methyl migration, bimolecular decomposition of the transient complexes and methyl transfer reactions, and such coverage cannot be repeated here and would

be beyond the scope of this contribution. Rather, here a selection of examples where use of hydrostatic pressure in kinetic studies enhances understanding of the mechanism will be presented.

In reactions of divalent transition metal ions with aliphatic free radicals, metal-carbon σ -bond formation is formally accompanied by oxidation of the MC:



Cobalt(II) and nickel(II) species reacted with $^X\text{CH}_3$ to produce intermediate species containing metal-carbon σ -bonds, a process characterised by a small positive ΔV^\ddagger , that indicated a dissociative interchange mechanism.^{295,296} Similar reactions of aquated Cr(II) ions with a series of 10 different aliphatic radicals exhibited an average ΔV^\ddagger of $+4.3 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$, also evidence for an I_d mechanism.²⁹⁷

Study of the formation and homolysis of $(\text{hedta})\text{Fe(III)-CO}_2^-$ and $(\text{hedta})\text{Fe(III)-CH}_3^-$ ($\text{hedta} = \text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)_2$) indicated three conclusions when these results were considered with other findings.²⁹⁸ They were first:

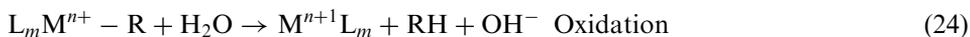


which proceeds by a ligand substitution mechanism. Second, homolysis of the metal-carbon bond follows the same mechanism, and third, ΔV^\ddagger for the homolysis reaction depends strongly on the nature of the central metal cation, i.e. the values are larger for $M^{n+1} = \text{Cr(III)}, \text{Co(III)}, \text{Ni(III)}$ and smaller for Fe(III) . It was also found that the volume of activation for the following reaction:



upon analysis demonstrated the role of changes in the electronic environment in terms of the coordination number and spin state of the complex during the formation and dissociation of the metal-carbon σ -bonds.

Heterolysis of the metal-carbon σ -bond in transient complexes of the type $L_m M^{n+1} - R$ produced as shown above can proceed by one of two alternative pathways in aqueous solution.^{299,300} One pathway involves formally an overall oxidation of the MC and the other reduction of the MC occurs during the reaction:



The kinetics of the heterolysis of several species containing Cr(III)-C σ -bonds have been studied at ambient pressure and at elevated pressures. In general the pathway followed was consistent with the oxidation pathway. Under different conditions the reactions were acid or general base catalysed. Volumes of activation for each component of the rate laws could be determined.³⁰¹ A particular conclusion that emerged was that water molecule bond cleavage could play an important role in the transition state. In one case this conclusion was based on interpretation of the magnitude of the H/D solvent isotope effect. These early studies were followed by posing the question were the mechanistic conclusions reached for the chromium systems applicable for other metal-carbon σ -bonds? Accordingly, the kinetics of the

heterolysis of the copper-carbon σ -bond in a complex of the type $[\text{LCu(II)-R}]^+$ ($\text{L} = 2,5,8,11\text{-tetramethyl-}2,5,8,11\text{-tetraazadodecane}$; $\text{R} = \text{CH}_2\text{CO}_2^-$) were examined at elevated pressures.²⁹⁸ Ambient pressure kinetics measurements earlier on this system had shown that the pathway followed is the oxidation pathway.^{302,303} In addition corresponding experiments were conducted for the decomposition of $[(\text{H}_2\text{O})_5\text{Cu(III)-R}]^{2+}$ ($\text{R} = \text{CH}_2\text{CO}_2^-$ or CHCl_2) systems which had been shown at ambient conditions to proceed by the reduction pathway.³⁰⁴ The volumes of activation for heterolysis of the Cu(III)-C σ -bonds of the complexes $[\text{Cu(III)-CH}_2\text{-CO}_2^-]^+$ and $[\text{Cu(III)-CHCl}_2]^{2+}$ were very different, -12.4 and $+10.4 \text{ cm}^3 \text{ mol}^{-1}$, respectively. The observed rate constants were not very different but the widely different volumes of activation required separate interpretation of the heterolysis process. For the former complex after examining and rejecting other hypotheses the following explanation was given. Bond formation with a solvent molecule in reductive heterolysis gave a transition state in which a water molecule binds to the carbon atom (of the metal-carbon bond) and shifts the M-C σ -bond electrons towards the MC thus causing its reduction. In addition, charge was formed during the process and could provide a contribution to the negative volume of activation. In contrast, the positive value of ΔV^\ddagger found for heterolysis of the $[\text{Cu(III)-CHCl}_2]^{2+}$ species was also explained, in part, by binding of a water molecule to the carbon atom, and also by induction of cleavage of a C-Cl bond. It was argued that a late transition state in which considerable C-Cl and M-C bond cleavage had already occurred, then these positive volume contributions will more than compensate for the volume reduction associated with C-O bond formation.

The transient complex $[\text{LCu(II)-CH}_3]^+$ decomposed according to a second-order rate law, and the volume of activation for that process was determined to be $-5 \text{ cm}^3 \text{ mol}^{-1}$. The reaction is:



After considering and rejecting other interpretations it was suggested that the mechanism was one in which formation of the transition state involved a coherent, partial C-C bond formation that will be associated with a volume collapse and a stretching of the Cu-C bonds. It was further suggested that the latter process will partially offset the volume collapse, but the C-C bond formation dominates in volume terms, consistent with a modest negative volume of activation.

Copper(I) complexes catalyse a variety of organic reactions which are of synthetic and industrial importance.³⁰⁵ In such processes that involve halide abstraction from aryl or alkyl halides, the abstraction step by a Cu(I) catalyst is believed to be the rate-determining step. In order to circumvent the property of facile disproportionation of Cu_{aq}^+ , various methods of stabilising Cu(I) and influencing reaction rates were considered.³⁰⁶ A kinetics study of ligand (L) effects on the reactivity of Cu(I)L complexes towards $\text{Cl}_3\text{CCO}_2^-$ was undertaken. The results indicated that the rate of the chlorine abstraction reaction was affected by several factors. These were the redox potential of the Cu(II/I)L couple, the hybridisation on Cu(I) in the Cu(I)L complex, steric hindrance, and electron density on the central Cu(I) cation at the binding site of the chlorine atom to be abstracted. The volume of activation,

distinctly negative, supported the expectation that the chlorine abstraction step proceeded by an associative mechanism.

5 Concluding remarks

Application of the hydrostatic pressure variable in a multitude of reaction kinetics studies leading to the volume of activation has been clearly demonstrated to be of inestimable value in mechanistic studies of organometallic chemistry reactions. Its relative simplicity of definition and precision of typical experimental values render the volume of activation to be of far superior mechanistic value than is the entropy of activation. The selection of reports described, a truly eclectic collection, illustrates that reactions of a wide range of metal-centred reactions have benefitted mechanistically from elevated pressure kinetics studies. Indeed in many cases the volume of activation adds that extra dimension to mechanistic elucidation. The breadth of techniques and variety of reaction monitoring methods described have added broader scope, interest and depth to this account.

Acknowledgements

We acknowledge the fact that several investigators have developed and applied high pressure technology in kinetics studies resulting in many interesting reports in this overall account. Colleagues who have contributed tirelessly to those reports from our own laboratories are also gratefully acknowledged. Financial support for the work performed in our laboratories came from the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

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