Coordination Chemistry Reviews, 25 (1978) 1—30

SOLVENT PATHS AND DISSOCIATE INTERMEDIATES IN SUBSTITUTION REACTIONS OF SQUARE-PLANAR COMPLEXES

R.J. MUREINIK

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem (Israel)

(Received 15 June 1977)

CONTENTS

A. INTRODUCTION

Substitution reactions of square-planar complexes have been extensively studied. The kinetics of reaction (1)

$$MA_3X + Y \rightarrow MA_3Y + X \tag{1}$$

are frequently described by a two-term rate equation (2)

$$\text{Rate} = k_{obs}[MA_3X] \tag{2a}$$

$$k_{obs} = k_s + k_y[Y] \tag{2b}$$

which has been interpreted in terms of the operation of two parallel associative reaction paths (3).

$$\begin{tikzcd}
& {[MA_3XS]} \arrow[r, "\text{fast}", "-X"'] & MA_3S \arrow[dr, "\text{fast}", "-S,\ +Y"'] & \\
MA_3X \arrow[ur, "k_s", "+S"'] \arrow[dr, "k_Y", "+Y"'] & & & MA_3Y \\
& {[MA_3XY]} \arrow[urr, "\text{fast}", "-X"'] & &
\end{tikzcd} \tag{3}$$

The substrate may undergo rate-determining associative attack either by the incoming ligand Y, or by a molecule of solvent S, in steps governed by the rate constants k_y and k_s, respectively. The five-coordinate species thus formed (which may be active intermediates or transition states) subsequently decay to product by the sequences of fast reactions shown above. The evidence on which the above-described mechanism is based has been reviewed by several authors [1—5], and will not be repeated here.

(i) The solvent path

Rate laws differing in form from eqn. (2) have been observed in numerous square-planar substitution systems. The most frequent exception to the two-term rate expression is the non-appearance of the term independent of the entering group. This may arise in a particular system because of the considerably greater reactivity towards the substrate of the ligand Y, compared with that of the solvent. The bulk of the reaction is then carried by the ligand path, i.e. $k_y[Y] >> k_s$. The absence of the solvent path in the rate law thus derives from the, essentially trivial but experimentally very important, statistical difficulty in detecting a small intercept (k_s) on a straight line of steep gradient (k_y).

In many cases, however, the solvolysis step is not as simple as represented above in the solvent path of (3). Solvolysis is frequently reversible and need not be rate determining in a reaction sequence proceeding via solvento intermediates. In this case the rate will be influenced by the presence of excess leaving group X, and the appearance of a term independent of Y will depend on the relative values of the rate constants of all the steps of the reaction path. A considerable amount of information concerning solvento species can be extracted from kinetic studies in which cognisance is taken of the reversible nature of the solvent path, and these data are discussed in section B.

(ii) Three-coordinate intermediates

The appearance of a k_s term in the rate law does not, per se, indicate that an associative path involving the solvent is operative, since such a term may arise from the rate-determining dissociation of the substrate giving a three-coordinate intermediate MA_3. Although the latter possibility has been discounted in the vast majority of cases for reasons discussed elsewhere [1—5], recent work has shown that in certain specific systems a dissociative mechanism does operate. The evidence for the kinetic participation of three-coordinate d^8 species is discussed in section C.

B. SOLVENTO INTERMEDIATES

(i) Reversible solvolysis

If the possibility of reversible solvolysis is considered, the mechanism becomes *

---

* For simplification the assumed five-coordinate intermediates in both paths are omitted. Since their decay to product is assumed to be fast, the kinetics are not affected by this simplification. Only in two cases has the formation of a stable five-coordinate intermediate been documented [6,7].

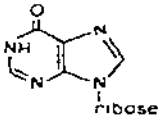
$$\begin{tikzcd}
MA_3X \arrow[r, shift left, "k_s;\, +S,\, -X"] \arrow[rr, bend right, "k_y;\, +Y,\, -X"'] & MA_3S \arrow[l, shift left, "k_{-s};\, +X,\, -S"] \arrow[r, "k_f", "+Y,\, -S"'] & MA_3Y
\end{tikzcd} \qquad (4)$$

As discussed below, the solvento species is often a highly reactive intermediate. Application of the steady state approximation to the solvento complex yields the overall rate eqn. (5)

$$k_{obs} = \frac{k_s k_f[Y]}{k_{-s}[X] + k_f[Y]} + k_y[Y] \qquad (5)$$

where the complex term represents the solvent path. This rather elementary kinetic form has been discussed in the context of square-planar substitution by several authors [8—12].

Seguin et al. [8] showed that the nucleoside derivative inosine (In)



replaces the bromide ligand in Pt(dien)Br$^+$ (dien = diethylenetriamine), at a rate governed by the expression

$$k_{obs} = \frac{k_s k_f[\mathrm{In}]}{k_{-s}[\mathrm{Br}] + k_f[\mathrm{In}]} + k_y[\mathrm{In}]$$

which corresponds to mechanism (4), with $k_y[\mathrm{In}]$ representing the ligand path, and the complex term the solvent path. The reaction of inosine with the palladium analogue, Pd(dien)Br$^+$, is more complicated in that reversibility has to be considered in the k_y path as well as for the reaction between inosine and the solvento complex [9]. In accordance with the mechanism

$$\mathrm{Pd(dien)Br^+ + In} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Pd(dien)In^{2+} + Br^-}$$

$$\mathrm{Pd(dien)Br^+ + H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Pd(dien)(H_2O)^{2+} + Br^-}$$

$$\mathrm{Pd(dien)(H_2O)^{2+} + In} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Pd(dien)In^{2+} + H_2O}$$

the rate eqn. (6) is observed. Kinetic parameters

$$k_{obs} = k_1[\mathrm{In}] + k_{-1}[\mathrm{Br^-}] + \frac{k_2 k_3[\mathrm{In}] + k_{-2}k_{-3}[\mathrm{Br^-}]}{k_{-2}[\mathrm{Br^-}] + k_3[\mathrm{In}]} \qquad (6)$$

were extracted from the experimental data by iterative procedures. The complexity of the Pd(dien)Br$^+$/inosine system was attributed to the very low reactivity of the ligand towards both the mother complex and its solvolysis product. This system appears to be the only one reported to date in which the full complexity of reversible stages occurring at comparable rates is encountered.

In an early study, the reaction of pyridine with *trans*-$Pt(PEt_3)_2RCl$, R = phenyl, *o*-tolyl, mesityl, was found to obey an equation of the form $k_{obs} = k_1 + k_2[py]$ and the variation of the rate constants with increasing steric hindrance provided early evidence of the associative nature of the substitution reaction [13]. Since the value of k_1 differed markedly from that observed when other nucleophiles were used, this reaction has been reinvestigated [10]. The kinetic data were interpreted in terms of a single reaction path proceeding via two equilibria involving the solvento intermediate

$$trans\text{-}Pt(PEt_3)_2RCl + MeOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{-}Pt(PEt_3)_2R(MeOH)^+ + Cl^-$$

$$trans\text{-}Pt(PEt_3)_2R(MeOH)^+ + py \underset{k_4}{\overset{k_3}{\rightleftharpoons}} trans\text{-}Pt(PEt_3)_2R(py)^+ + MeOH$$

which gives $k_{obs} = \dfrac{k_1[py] + k_4(k_2/k_3)[Cl^-]}{(k_2/k_3)[Cl^-] + [py]}$.

The value of k_3 was measured independently in a separate kinetic study of the reaction of *trans*-$Pt(PEt_3)_2R(MeOH)^+$ with pyridine. The value of k_1 so obtained was in good agreement with that found for other ligands, for R = *o*-tolyl and mesityl, but agreement was only fair for R = phenyl. The authors suggest that since the phenyl compound is the least sterically hindered of this class of compounds, it is possible that a ligand path also operates. For the *o*-methyl substituted derivatives, the steric hindrance suppresses the ligand path. These studies have been extended with similar results to other solvents [11] and to substituted pyridines as entering groups [12].

Reactions in which the ligand path does not separate, and in which the formation of the solvento complex is reversible, have been reported. The reaction between the olefin complex $Pt(ol)Cl_3$ (ol = allyl NH_3^+, allyl PEt_3^+, allyl SO_3^-, pent-4-enyl NH_3^+) and bipyridyl (bipy) produces $Pt(bipy)Cl_2$ in a single observed process [14]. The kinetics were found to obey the rate law $1/k_{obs} = k' + k''[Cl^-]/[bipy]$ which was interpreted as reflecting the mechanism

$$Pt(ol)Cl_3 + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pt(ol)Cl_2(S) + Cl^-$$

$$Pt(ol)Cl_2(S) + bipy \xrightarrow{k_2} Pt(bipy)(ol)Cl + S + Cl^-$$

$$Pt(bipy)(ol)Cl + Cl^- \xrightarrow{fast} Pt(bipy)Cl_2$$

with $k' = 1/k_1$ and $k'' = k_{-1}/k_1k_2$. The chloride ion undergoing solvolysis in the first step must be the ligand *trans* to the highly labilising olefin, so that direct substitution of olefin and S cannot occur in the same step, since the *cis* geometry of the final product is predicated by the bidentate nature of bipyridyl. Support for the nature of the intermediate, Pt(bipy)(ol)Cl, comes from the reaction of the related compound $Pt(ac)Cl_3^-$ (ac = 2,5-dimethyl, 3 hexyne, 2,5-diol) [15]. In this case, the reaction proceeds in two discernible stages with the second sufficiently slow that the product of the first stage can be isolated and shown to be the cation $Pt(bipy)(ac)Cl^+$. Similar kinetic results were obtained for the reaction of bipyridyl with $Pt(CO)Cl_3^-$ [16] and with Zeise's anion $Pt(C_2H_4)Cl_3^-$ [17]. The rapidity of the displacement of olefin from Pt(bipy)(ol)Cl in the case of the olefins bearing a charged substituent was related to the solubilising nature of that group, but no reasons were advanced [14].

The leaving group also competes effectively with the entering group for the solvento intermediate in the reaction between oxalate ions (ox) and *cis*-$Pt(NH_3)_2Cl_2$ [18]. This reaction is governed by the following mechanism

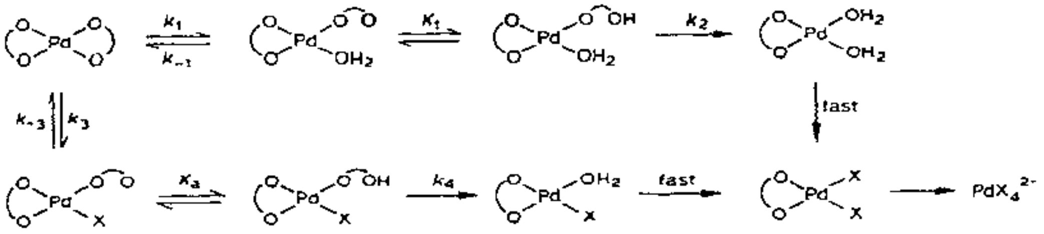
$$cis\text{-}Pt(NH_3)_2Cl_2 + H_2O \underset{k_b}{\overset{k_a}{\rightleftharpoons}} cis\text{-}Pt(NH_3)_2(H_2O)Cl^+ + Cl^-$$

$$cis\text{-}Pt(NH_3)_2(H_2O)Cl^+ + ox \xrightarrow{k_c} cis\text{-}Pt(NH_3)_2(ox)$$

with

$$k_{obs} = \frac{k_a k_c [ox]}{k_b [Cl^-] + k_c [ox]}$$

Reversibility of both solvent and ligand paths was considered in a related system, the hydrolysis and substitution reactions of $Pd(acac)_2$ (acac = acetylacetonate) [19]. The following overall mechanism was suggested



In the absence of added nucleophile X, only the reactions in the top line of the mechanism occur. The hydrolysis is thus governed by the rate law (7),

$$k_{obs} = k_1 k_2 K_1 [H^+]/(k_{-1} + k_2 K_1 [H^+]) \tag{7}$$

which differs from the mechanisms discussed above only in the fast protonation equilibrium that traps the free end of the chelate. When another nucleophile is present as well, the whole mechanistic scheme applies, and eqn. (7) is now expanded by the addition of another term of similar form, $k_3 k_4 K_a$-$[H^+][X^-]/(k_{-3} + k_4 K_a [H^+])$.

Reinhardt and Monk [20] interpreted the kinetics of the reaction of ammonia with $PdCl_4^{2-}$ in terms of mechanism (4) described above, but introduced a simplifying approximation. The solvent term in (5) can be expressed as

$$\frac{k_s[\mathrm{Y}]/[\mathrm{X}]}{k_{-s}/k_f + [\mathrm{Y}]/[\mathrm{X}]} \qquad (8)$$

from which it can be seen that the appearance of the concentration ratio of the incoming and leaving groups in the rate law depends on the relative magnitudes of the rates of anation. If the solvento complex reacts much slower with the incoming group than with the departing ligand, the solvent term will reduce to $k_s k_f[\mathrm{Y}]/k_{-s}[\mathrm{X}]$. This behaviour was found for the reaction between $PdCl_4^{2-}$ and NH_3 which takes place in two observable stages. Both steps obey rate expressions of the form

$$k_{obs} = k_y\{[NH_3]/[Cl^-]\}\{r_y + [Cl^-]\}$$

where the term in $k_y r_y$ corresponds to the solvent path. For the reaction in the reverse direction [21], the rate expression is of the more familiar two-term type, $k_{obs} = k_1 + k_2[Cl^-]$, representing the other possible extreme approximation in (8), namely, the rate of reaction of the solvento complex with the incoming ligand is fast.

It should be noted that this corresponds to the frequent designation of the solvento species as a highly active intermediate, although, as seen here and as discussed below, this is by no means always a valid generalization. Under circumstances in which the solvolysis path is operative and reversibility is not an important consideration, the observed value of the ligand-independent term should be identical with the rate of solvolysis in the absence of the substituting ligand. This has generally been found to be the case [22—28] (however, see below) and quite frequently only the solvent path operates, so that all substitution proceeds via the solvento intermediate [29].

If $k_{-s}[\mathrm{X}] << k_f[\mathrm{Y}]$, the mechanism is essentially (3), and a necessary condition is that the rate of reaction of the solvento species with Y be greater than the measured rate in the solvent path. This has been verified in a number of cases in which it was possible to prepare the solvento complex independently of the reaction under study, and to measure its rate of reaction with various nucleophiles. Thus, Banerjea et al. [30] demonstrated that the solvolysis products of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$, $Pt(en)Cl_2$ and $Pt(NH_3)_3Cl^+$ reacted faster with various nucleophiles than did the parent chlorocomplexes. Similarly, Cattalini et al. [31] showed that $AuCl_3(MeOH)$ reacts with a variety of amines faster than $AuCl_4^-$. More recently, Coe and Lyons [32] investigated the reaction of $Pd(dien)(NH_3)^{2+}$ with chloride ion, and found that the aquo intermediate $Pd(dien)(H_2O)^{2+}$ was sufficiently reactive toward both ammonia and chloride to be an intermediate in the reaction.

In an early study, Gray and Olcott [33] showed that $Pt(dien)(H_2O)^{2+}$ reacted with various ligands at a sufficient rate to serve as an intermediate in the reactions of $Pt(dien)X^+$ with these nucleophiles. However, the rate of reaction of $Pt(dien)(H_2O)^{2+}$ with nucleophiles Y obeys the relation $k_{obs} = k_1 + k_2[\mathrm{Y}]$.

Since the substrate in this case is a solvento species, this k_1 cannot be attributed to a reaction path involving rate-determining associative formation of a solvento intermediate. The nature of k_1 in these systems does not seem to have been investigated further, but it appears likely that k_1 represents a dissociative reaction path of considerably less importance than the usual associative mode of reaction. Since these reactions were reported to go to completion, k_1 cannot arise from the dissociation of Pt(dien)Y^+ in a reversible anation. Evidence for dissociative activation is discussed in section C.

Bekker and Robb [34] discussed the conditions under which mechanism (4) yields a simplified equation. In addition to the case discussed above, namely, $k_f[Y] >> k_{-s}[X]$, a two-term rate law may be obtained when these two reaction rates are comparable, i.e., $k_f[Y] \sim k_{-s}[X]$. Under these conditions $k_2 = k_y$ but $k_1 \sim \frac{1}{2}k_s$. Rate plots of k_{obs} against [Y] will then yield a family of lines which, unlike the simple mechanism (3), do not necessarily share a common intercept. The values of k_1 will depend on the nature of Y. An example of such behaviour appears to have been observed for the substitution reactions of Rh(cod)(pip)Cl with various amines [35] (cod = 1,5 cyclooctadiene; pip = piperidine). Unpublished work in our laboratory [36] has shown that terpyridyl complexes of platinum behave similarly.

For the reaction of $PdCl_4^{2-}$ with thiourea [34], no direct evidence for a solvent path was observed, even in solutions known to contain significant amounts of $PdCl_3(H_2O)^-$. The aquo complex is considerably more reactive towards *o*-phenanthroline [37,38] and monobasic amines [39] than $PdCl_4^{2-}$. However, the strong reactivity of thiourea towards d^8 complexes has been demonstrated to derive, at least in part, from a certain measure of ability to absorb electron density in π back donation [40,41]. For such biphilic ligands, increase in the total charge of the substrate can result in a reduction of ligand reactivity by moderating the availability of π electron density on the metal. Invoking these arguments and previous observations that thiourea appears to be unreactive towards hydrolysed metal ions [42], Bekker and Robb [34] argued that comparable values of k_y and k_f apply in this system. Independent knowledge of the rates of hydrolysis and anation of $PdCl_4^{2-}$ [43] enabled them to calculate that in this particular system the solvent path contributes only about 2% of the total measured reaction.

The non-appearance of the solvent term may thus be rationalised in terms of a detailed analysis of mechanism (4) although a chemical explanation may not always be apparent. Mureinik [44] studied the reaction of thiocyanate ion with $PtCl_4^{2-}$ in fresh solutions of complex, and in solutions that had been allowed to attain hydrolytic equilibrium with respect to $PtCl_3(H_2O)^-$. No evidence was found for kinetic participation of the aquo complex even under conditions in which up to one-fifth of the total platinum was present as the aquo complex. Since the yield of product was always quantitative, the aquo complex initially present must anate to the tetrachloro compound before undergoing reaction with thiocyanate. Analysis of the system in terms of the rates of the hydrolysis and anation steps (k_s, k_{-s} respectively) for $PtCl_4^{2-}$

[45—47] showed that this is compatible with the observed kinetic data. The reason for the apparent inertness of thiocyanate towards $PtCl_3(H_2O)^-$ is not clear; biphilic properties, which have been demonstrated towards Au(III) substrates [41] but, significantly, not towards Pt(II) substrates [40] may be responsible. This explanation was tentatively suggested to account for the non-participation of a solvent path in the reaction between $PtCl_4^{2-}$ and the allylammonium ion [48]. In this study the rate of reaction was found to be independent of the concentration of aquo complex in the pre equilibrated complex solution, but only a very limited concentration range was considered, For olefins, π back donation of electron density of the metal to anti-bonding orbitals of the ligand is an essential component of the bond. Contraction of the d-orbitals on the platinum atom in the higher charged aquo complex reduces the ease of bonding and renders the olefin inert towards $PtCl_3(H_2O)^-$. Green and Wilson [49] observed similar inertness of the aquo complex towards ethylene and suggested the formation of an outer sphere complex between $PtCl_4^{2-}$ and ethylene, in which steric and electronic factors prevent solvent attack.

Other instances of non-reactivity of solvento species have been noted, but the phenomenon is not yet sufficiently well documented to enable generalisations to be made regarding its chemical origins. Teggins et al. [23,50] showed that diethylenetriamine (dien) reacts with $PtCl_4^{2-}$ and $PtBr_4^{2-}$ exclusively by ligand paths under conditions in which the trihaloaquo complex would be expected to be kinetically important. On the other hand, the reaction of 1,3-propanediamine (pd) with $PtCl_4^{2-}$ takes place via both ligand and solvent paths [51], where the rate constant governing the latter route is in good agreement with independent determinations of the rate of hydrolysis of $PtCl_4^{2-}$ [45—47]. In the reaction of $Pt(pd)Cl_2$ with pd, however, there is no evidence for a solvent path, although on the basis of the rate of hydrolysis of the similar complex $Pt(en)Cl_2$ [28,30] such a mechanistic step would be expected. Related observations include the low reactivity of $Pt(dien)(OH)^+$ towards ammonia [32] and the inertness of complexes of the type $Pt(NH_3)_2Cl(OH)$ towards ammonia [52]. Further work in this direction is indicated.

The use of pre-equilibrated solutions in systems in which the reaction via rate-determining solvolysis does occur, yields a different form of kinetic behaviour. Complexes of the type Rh(COD)(am)Cl (COD = 1,5 cyclooctadiene, am = amine) were allowed to attain solvolytic equilibrium in methanol before being treated with bipyridyl [53]. The reaction yields $Rh(COD)(bipy)^+$ via two different observable processes, the slower of which obeys the usual form $k_{obs} = k_1 + k_2[bipy]$. The kinetics of the fast reaction were not measured, but it was noted that the fraction of the overall reaction that proceeds by the fast process decreases with increasing base strength of am, i.e., as the bond strength Rh—am increases. The mechanism suggested resembles those described above, except that the amine ligand is displaced in the solvolytic step.

$$\begin{tikzcd}
\mathrm{Rh(COD)(am)Cl} + \mathrm{MeOH} \arrow[rr, shift left, "k_s"] \arrow[dr, "k_y", "{+\mathrm{bipy}, -\mathrm{am}, -\mathrm{Cl}^-}"'] & & \mathrm{Rh(COD)Cl(MeOH)} + \mathrm{am} \arrow[ll, shift left, "k_{-s}"] \arrow[dl, "k_f"', "{+\mathrm{bipy}, -\mathrm{MeOH}, -\mathrm{Cl}^-}"] \\
& \mathrm{Rh(COD)(bipy)} &
\end{tikzcd}$$

At the time of initiation of the reaction, all the rhodium initially present as methanolo complex undergoes fast reaction governed by k_f, after which the classic mechanism of parallel rate-determining solvolysis and ligand attack apply for the reaction of the remainder of the starting material. Similar behaviour was observed for the reaction of *trans*-$\mathrm{Pt(py)_2Cl_2}$ with various nucleophiles in dimethyl sulfoxide (DMSO) and aqueous DMSO [54], and for the reaction of *trans*-$\mathrm{Pt(SEt_2)_2I_2}$ with ammonia in ethanol or benzene solution [55].

(ii) Fast pre-equilibrium solvolysis

When the reaction of the solvento complex with the incoming group is slow compared with the rate of attainment of solvolysis equilibrium, i.e., the solvolysis is a rapidly attained pre-equilibrium, the rate is determined by the interaction between the incoming group, and each of the two complexes $\mathrm{MA_3X}$ and $\mathrm{MA_3S}$.

$$\begin{tikzcd}
\mathrm{MA_3X} + \mathrm{S} \arrow[rr, shift left, "K_{S,\mathrm{fast}}"] \arrow[dr, "k_y", "{+\mathrm{Y}, -\mathrm{X}}"'] & & \mathrm{MA_3S} + \mathrm{X} \arrow[ll, shift left] \arrow[dl, "k_f"', "{+\mathrm{Y}, -\mathrm{S}}"] \\
& \mathrm{MA_3Y} &
\end{tikzcd} \tag{9}$$

The complete rate equation is

$$k_{\mathrm{obs}} = \frac{K_s k_f + k_y[\mathrm{X}]}{K_s + [\mathrm{X}]}\,[\mathrm{Y}] \tag{10}$$

and pure first order behaviour in Y is observed. The existence of a solvent path must be deduced from the rate dependence on the concentration of the leaving group. Frequently the extent of hydrolysis is small (either intrinsically so, or under control of large amounts of X) so that eqn. (10) reduces to

$$k_{\mathrm{obs}} = (K_s k_f/[\mathrm{X}] + k_y)[\mathrm{Y}] \tag{11}$$

where the term in X represents reaction via the solvento species.

Behaviour of the type described by (9) and (10) was observed by Rund and co-workers for the reactions of the tetrahalocomplexes of platinum and palladium with bipyridyl and *o*-phenanthroline (phen) [25,37,38,56—58]. The reaction of phen with $\mathrm{PtCl_4}^{2-}$ proceeds via its rate-determining attack on both the tetrachlorocomplex and its hydrolysis product [37,38,58],

$$\begin{tikzcd}
\mathrm{PtCl_4}^{2-} + \mathrm{H_2O} \arrow[rr, shift left, "K_{\mathrm{fast}}"] \arrow[dr, "k_y", "{+\mathrm{phen}, -2\,\mathrm{Cl}^-}"'] & & \mathrm{PtCl_3(H_2O)}^- + \mathrm{Cl}^- \arrow[ll, shift left] \arrow[dl, "k_f"', "{+\mathrm{phen}, -\mathrm{Cl}^-, -\mathrm{H_2O}}"] \\
& \mathrm{Pt(phen)Cl_2} &
\end{tikzcd}$$

according to the rate equation $k_{\mathrm{obs}} = \left\{\dfrac{k_t K + k_y [\mathrm{Cl}^-]}{K + [\mathrm{Cl}^-]}\right\} [\mathrm{phen}]$.

The reaction is insensitive to acid concentration at pH values close to pK_a for the incoming ligand, but does show the ionic strength effects to be expected for reaction between oppositely charged species. This suggests that the active form of the ligand is the protonated base, phenH^+. The reaction is greatly influenced by the nucleophilic character of the amine, with more basic substituted phenanthrolines reacting faster. The slowness of reaction between the complex species and phen was related to the rigidity of the amine molecule, since the reaction of bipy with $\mathrm{PtCl_4}^{2-}$ is five times faster than that of the equally basic 5,6 dimethylphenanthroline. The greater rigidity of the phenanthroline skeleton, in contrast to that of bipy where free rotation about the axis joining the two pyridine nuclei is possible, must impose considerable steric limitations on the reacting species in the attainment of a fruitful encounter orientation appropriate to the formation of the transition state. Reactions in which stringent orientation requirements are imposed are generally slow, the increased ordering required being reflected in activation entropies considerably more negative than those for systems where the direction of approach of the ligands is less crucial [59—61].

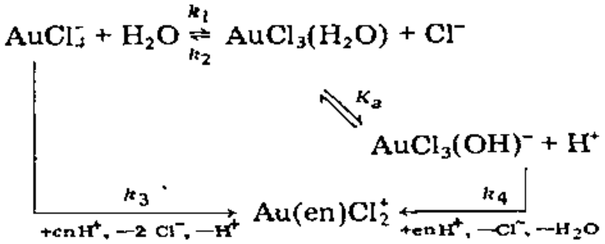
The ratio of the rates of reaction of $\mathrm{PtCl_4}^{2-}$ with phen, bipy and ethylenediamine (en) is 1 : 3 : 100 [37], although this comparison is not entirely valid since the mechanism of the en reaction is probably different. * The next higher homologue in the aliphatic diamine series was shown to react via rate-determining solvolysis in the solvent path [51], and it is likely that the same will be true for en as well. These highly flexible bidentate ligands are sufficiently reactive to prevent the hydrolysis equilibrium being maintained during the course of the reaction. Similar kinetic behaviour was obtained for the reaction of phen with other $\mathrm{MX_4}^{2-}$ complexes [M = Pd, Pt; X = Cl, Br, I) [38,57,58] and for the reaction of bipy with $\mathrm{PtCl_4}^{2-}$ and $\mathrm{PdCl_4}^{2-}$ [25]. From the kinetic data values of the solvolysis equilibrium constant were extracted and found to be in good agreement with values measured independently [30,65], thus providing supporting evidence for mechanism (9). It is relevant that the kinetic data revealed that the aquo complex, $\mathrm{MX_3(H_2O)}^-$ is more reactive than the parent species $\mathrm{MX_4}^{2-}$, as may have been anticipated in the light of the discussion in the previous section. Interestingly, when the reaction was conducted at pH values that would cause deprotonation of the coordinated water molecule, the resultant hydroxo complex was found to be more reactive than its conjugate acid [38,57]. This behaviour which stands in contrast to the non-reactivity of the hydroxo complexes $\mathrm{Pt(dien)(OH)}^+$ and $\mathrm{Pt(NH_3)_2Cl(OH)}$ with ammonia [32,52], is not understood. An explanation may possibly be sought in the unusual reactions at the α-carbon atom of coordinated bipy and

---

* Although the reaction between $\mathrm{PtCl_4}^{2-}$ and en has been studied [62—64], the overall mechanism in general, and the solvent path and hydrogen ion dependence in particular, were not adequately investigated.

phen ligands recently described by Gillard et al. [66—68]. When the reaction between phen and $PtCl_4^{2-}$ is conducted in mixed solvents, the kinetics are more complex [56]. An induction period is observed, and the rate is independent of the concentration of the base. Higher solvento species, including possibly mixed solvento complexes appear to be involved.

The tetrachlorocomplexes of palladium and gold are considerably more reactive than their platinum analogue, so that for $PdCl_4^{2-}$ and $AuCl_4^-$ the hydrolysis equilibrium is maintained during the course of reaction even with reactive aliphatic chelating amines [69—74]. Robb and co-workers investigated the reactions of en and *N*-substituted ethylenediamines with $AuCl_4^-$ [69,71,72]. The aquo complex, $AuCl_3(H_2O)$ is a fairly strong acid [75], and in the pH region investigated is extensively deprotonated. The kinetics of the reaction between $AuCl_4^-$ and en were interpreted in terms of the following mechanism [71]



(12)

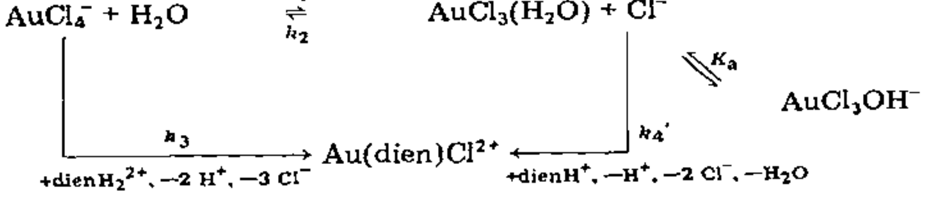
which yields the following expression

$$k_{obs} = \{k_3K_a'/[H^+] + k_1k_4K_aK_a'/k_2[Cl^-][H^+]^2\}[enH_2^{2+}] \qquad (13)$$

where K_a' is the first acidity constant for the diprotonated en cation

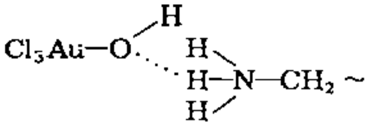
$$enH_2^{2+} \overset{K_a'}{\rightleftharpoons} enH^+ + H^+$$

In the pH range investigated no free en exists and a factor of $1/[H^+]$ in each term of (13) derives from the protonation equilibrium for enH_2^{2+}. The hydrolysis of the aquo complex (K_a) introduces the second factor $1/[H^+]$ into the second term of (13), which thus represents behaviour of the type described by (11) with $k_1/k_2 = K_s$. An analogous expression was found for the reaction of $AuCl_4^-$ with dien at pH values less than 4.4, where K_a' of (13) is replaced by the first acidity constant for the $dienH_3^{3+}$ ion [70]. The form of the observed rate equation does not differentiate between a mechanism of the type (12) and the alternate formulation



where the hydroxo complex has no kinetic role. The inverse square dependence on $[H^+]$ would arise from the reaction between the aquo complex and the doubly deprotonated base, dienH^+. This kinetically equivalent form was discarded on the basis of the values thus obtained for the individual rate constants, which would have dienH^+ some 10^7 more reactive than dienH_2^{2+} in contrast to the factor of 5 obtained by Teggins and Woods for the reaction of dien with $PtBr_4^{2-}$ [50].

The reactivity of $AuCl_3(OH)^-$ as opposed to the kinetic inertness of its conjugate acid was attributed to the ability of the coordinated hydroxy ligand to form a hydrogen bond to an NH_3^+ group of the protonated amine [70],



This facilitates the departure of the hydroxo leaving group. Less acidic aquo complexes such as $PtBr_3(H_2O)^-$ and $PtCl_3(H_2O)^-$ are not deprotonated under similar conditions [23,50], and hence the coordinated water molecule cannot be labilised in this way. Comparison of the values of the discriminating power of $AuCl_4^-$ towards en and dien with those obtained for a series of *N*-methyl substituted ethylenediamines [72] suggests that the central nitrogen in dien is involved in the first deprotonation equilibrium. In keeping with the hydrogen bonding hypothesis above, k_4 for dienH_2^{2+} with two NH_3^+ groups, was found to be approximately double that for enH^+ with only one such group.

For the *N*-substituted ethylenediamines [70], totally first order dependence on $[\text{amH}_2^{2+}]$ is observed, but the chloride dependence of both terms is different, the observed rate law taking the form

$$k_{\text{obs}} = \{a[\text{Cl}^-]/[\text{H}^+] + b/[\text{H}^+]^2\}[\text{amH}_2^{2+}] \qquad (14)$$

as if the whole right hand side of (13) were multiplied by $[\text{Cl}^-]$. It was suggested that the ion pair $\text{amH}^+ \cdot \text{Cl}^-$ participates in the substitution reaction in place of amH^+ in mechanism (12). This yields rate eqn. (14) with $a = k_3K_a'K_{ip}$ and $b = k_1k_4K_aK_a'/k_2$, where K_{ip} is the equilibrium constant for the formation of the ion pair, $\text{amH}^+ + \text{Cl}^- \overset{K_{ip}}{\rightleftharpoons} \text{amH}^+ \cdot \text{Cl}^-$. Evidence for extensive ion pairing for the substituted diamines was obtained from conductometric measurements.

The reactions of $PdCl_4^{2-}$ with en and its derivatives were investigated by de Waal and Robb [73,74]. The aquo complex $PdCl_3(H_2O)^-$ resembles its platinum rather than its gold analogue in acid properties, leading to simplified hydrogen ion dependence. However, when the reaction is conducted in acetate-buffered media, an acetato complex is also formed. The observed rate law is of the form (15)

$$k_{\text{obs}} = \{k_c/[\text{H}^+] + k_d/[\text{H}^+][\text{Cl}^-] + k_e[\text{OAc}^-]/[\text{H}^+][\text{Cl}^-]\}[\text{en}_{\text{total}}] \qquad (15)$$

The first two terms resemble the rate law for the reaction of $AuCl_4^-$ except for the absence of the factor $1/[H^+]$ in the k_d term which derives from the acidity of $AuCl_3(H_2O)$. The mechanism suggested is an obvious extension of those discussed above.

$$PdCl_4^{2-} + H_2O \xrightleftharpoons{K,\ \mathrm{fast}} PdCl_3(H_2O)^- + Cl^-$$

$$PdCl_3(H_2O)^- + OAc^- \xrightleftharpoons{K',\ \mathrm{fast}} PdCl_3(OAc)^{2-} + H_2O$$

$$enH_2^{2+} \xrightleftharpoons{K_a} enH^+ + H^+$$

$$\begin{tikzcd}
PdCl_4^{2-} \arrow[r, rightleftharpoons, "K"] \arrow[dr, "k_1", "{+enH^+, -H^+, -2\,Cl^-}"'] & PdCl_3(H_2O)^- \arrow[r, rightleftharpoons, "K'"] \arrow[d, "k_2"', "{+enH^+, -Cl^-, -H^+, -H_2O}"] & PdCl_3(OAc)^{2-} \arrow[dl, "k_3"', "{+enH^+, -Cl^-, -HOAc}"] \\
 & Pd(en)Cl_2 &
\end{tikzcd} \qquad (16)$$

This scheme yields the rate expression (15) where $k_c = k_1K_a$; $k_d = k_2K_aK$; $k_e = k_3K_aKK'$.

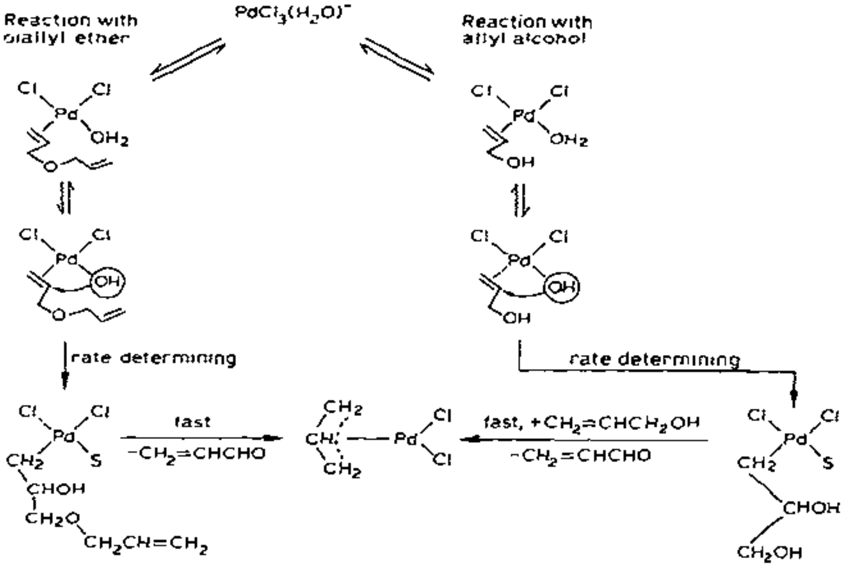
The reactions of $PdCl_4^{2-}$ with *N*-methyl substituted diamines in the absence of buffering agents obeys the rate expression

$$k_{obs} = \{k/[H^+] + k'/[H^+][Cl^-]\}[en_{total}]$$

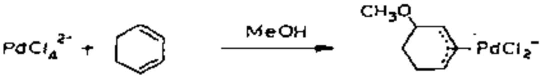
in agreement with the appropriate part of mechanism (16) above. The "migration" of the term $[Cl^-]$ to the numerator of the first term and its disappearance from the second term of eqn. (15) only occurs for the most highly substituted base studied, namely, *N,N,N',N'*,-tetramethylethylenediamine, and this only at high chloride concentrations. This obvious disparity between the gold and palladium systems does not appear to be easily reconciled, since ion-pairing in the ligand must be independent of the metal ion undergoing reaction. Furthermore, it is not clear why the ion pair formed with amH^+ ion influences the kinetics, while no evidence was obtained for the more probable pairing between chloride and the doubly charged cation amH_2^{2+}.

Hydrolysis reactions of $PdCl_4^{2-}$ are believed to participate in many palladium-catalysed processes involving the oxidation of unsaturated hydrocarbons [76,77]. In a number of reactions between olefinic ligands and $PdCl_4^{2-}$ the reaction does not proceed as far as complete oxidation of the olefin, and the final product is an organometallic complex. Both allyl alcohol [78] and diallyl ether [79] react with $PdCl_4^{2-}$ in aqueous methanol forming $(h^3\text{-}C_3H_5)\cdot PdCl_2^-$ and vinyl aldehyde. For both reactions the rate law is $k_{obs} = k[\mathrm{all}]/[H^+][Cl^-]^2$, where all represents the appropriate allyl compound. The value of k for diallyl ether is approximately double that for allyl alcohol. Only one term appears in the rate expression suggesting that the tetrachloro complex itself is kinetically inactive. The following mechanism is believed to apply:

$PdCl_4^{2-} + H_2O \rightleftharpoons PdCl_3(H_2O)^- + Cl^-$



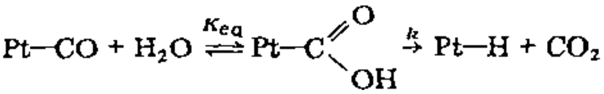
The rate-determining step is attack by coordinated hydroxide on the β carbon atom of the coordinated olefinic linkage, followed by fast rearrangement to the π-allyl complex, accompanied by elimination of vinyl aldehyde. The statistical factor derived from the presence of two olefinic groups per molecule in the ether explains the relationship between the rate constants for the two allyl compounds. A π-allyl compound [80] is also formed when $PdCl_4^{2-}$ reacts with 1,3 cyclohexadiene, but the rate law differs in form and solvento intermediates are not postulated.



There are frequent instances of solvent participation in the kinetics of reactions which may be stoichiometrically regarded as substitution reactions, but which are shown by mechanistic considerations to be subtly different. Solvent participation in such reactions does not imply solvolysis in the sense of formation of solvento intermediates. An example is the formation of metal hydrides by the action of acid on carbonyl complexes [81]. The reaction

trans-$Pt(PEt_3)_2(CO)Cl + H_2O \rightarrow$ *trans*-$Pt(PEt_3)_2(H)(Cl) + CO_2$

was found to obey the rate equation $k_{obs} = a/[H^+]$ and the following schematic mechanism was suggested.



$$Pt{-}CO + H_2O \overset{K_{eq}}{\rightleftharpoons} Pt{-}C\begin{matrix}{\scriptstyle //O}\\{\scriptstyle \backslash OH}\end{matrix} \overset{k}{\rightarrow} Pt{-}H + CO_2$$

The constant a is given by $a = K_{eq}k$, and although the solvent is essential for the reaction, the reaction is at the coordinated ligand and solvolysis is not involved.

(iii) Nature of the solvent

The extent and ease of solvolysis is dependent on the nature of the solvent. Variation of the solvent has been extensively employed to study the influence of solvation on the ligand path [82—89]. However, the results are not always unambiguous for the k_1 term because of the dual role of the solvent as nucleophile and reaction medium in this mechanistic route.

In one of the earliest systematic studies of solvent effects [82] it was found that no solvent path operated in the exchange of isotopic chloride ion with coordinated chloride in *trans*-Ptpy$_2$Cl$_2$, when the reaction was conducted in poor solvating agents such as CCl_4, ethylacetate, 1,2-dichloroethane and benzene. On the other hand, in good solvating media such as DMSO, CH_3NO_2, C_2H_5OH and water, the k_1 path does operate. Surprisingly, no solvent path was observed in dimethyl formamide (DMF) or CH_3CN, although the inherently substantial experimental error involved in measuring isotopic exchange rates may have been partly responsible. For the reaction of *trans*-Pt(pip)$_2$Cl$_2$ (pip = piperidine) with various nucleophiles, k_1 decreased in the order DMSO > acetone > DMF > CH_3CN > CH_3NO_2 > CH_3OH [84]. The solvent path for the reactions of *trans*-Pt(pip)$_2$(NO$_2$)$_2$ in CH_3OH played a considerably less important role than in DMSO or DMF [86]. For the latter solvent, k_1 was in fact two orders of magnitude greater than the value observed in CH_3OH. Drago et al. [85] showed that at least two factors, the donor strength and the general solvating ability of the solvent, must be considered in determining the relative importance of the solvent path in any particular system. Labelled chloride exchanges with *trans*-Pt(py)$_2$Cl$_2$ in DMSO by the ligand path only, but is zero-order in [Cl$^-$] in $CDCl_3$. NMR spectra show that the ground state of the complex is the same specifically solvated species in a 1 : 9 mixture of DMSO and $CDCl_3$, as in pure DMSO. However, in the mixed solvent, reaction occurs via a path first-order in [Cl$^-$]. Were the specific donor ability of the solvent the sole governing factor, the same mechanism would apply in DMSO as in the mixed solvent. That it does not, indicates that general solvating properties, i.e., the ability of the solvent to facilitate charge separation and stabilise the incipient charged species, are important. Similarly, reaction in the good general solvator and relatively poor donor, sulfolane, goes entirely by the solvent route, whereas in the strongest donor investigated, pyridine, a first-order term in chloride was observed.

Hupp and Dahlgren [89] recently investigated the solvent path for the reaction of *trans*-Pt(ol)(am)Cl$_2$ with 1-pentene (ol = styrene, am = p-substituted aniline). In pure $CHCl_3$, the rate expression $k_{obs} = k_1 + k_2$[pentene] was obeyed with k_1 frequently indistinguishable from zero. The solvent path is highly unfavoured since chloroform is a non-coordinating solvent. However, when small amounts of ethanol were added, the k_1 path assumed considerable significance while the rate via the ligand path decreased. The appearance of the k_1 path on addition of ethanol was attributed to strong solvation by the alcohol, although no distinction could be drawn between general solvation or specific z-axis interaction, i.e., donor behaviour at the most accessible potential coordination site. The retardation of the ligand path was attributed to greater difficulty in attaining the transition state because of the need to displace solvating ethanol molecules(s).

Most studies concerning the properties of the solvent deal with specific aspects of mixed solvents, and are more appropriately discussed in the separate section below.

C. DISSOCIATIVE MECHANISMS

The presence of a term in the rate law independent of the incoming group does not of course constitute proof of the participation of a solvolytic intermediate, and rate-determining cleavage of the bond M—X in the scheme

$$MA_3X \xrightarrow[-X]{k} MA_3 \xrightarrow[+Y]{\text{fast}} MA_3Y$$

will result in indistinguishable kinetics. This chapter discusses the evidence for such dissociative mechanisms.

(i) Complexes of 1,1,7,7-tetraethyldiethylenetriamine (Et₄dien)

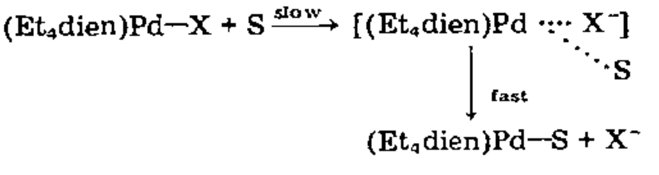
A dissociative mechanism seems to have been first postulated for square-planar systems by Basolo and Pearson [1] for the reactions of the highly hindered complex $Pt(Et_4dien)Cl^+$ with various nucleophiles. Whereas complexes of the unsubstituted triamine, $Pt(dien)X^+$, reacted with various nucleophiles in accordance with the usual rate law, $k_{obs} = k_1 + k_2[Y]$, introduction of the four ethyl groups drastically reduced the overall rate and totally suppressed the ligand path. Molecular models show that the alkyl substituents essentially block approach to the metal along the direction perpendicular to the plane of the complex. These highly hindered molecules were termed pseudo-octahedral complexes. It was suggested that their reactions departed from the conventional behaviour for square-planar substrates, and that they occurred by the S_N1 mechanism typical of octahedral cobalt(III) complexes.

Most subsequent studies of Et_4dien complexes have dealt with palladium or gold rather than platinum, probably because of their more conveniently measurable rates of reaction. Kinetics independent of the nature and concentration of the incoming ligand were observed for many reactions of $Pd(Et_4dien)X^+$ (X = halide) [90—92] and individual reasons were advanced for each incoming group that departed from this pattern. The k_2 terms observed for OH^- and $S_2O_3^{2-}$ were ascribed to the operation of a conjugate base (S_N1CB) mechanism [90] and to the extremely high nucleophilicity of $S_2O_3^{2-}$ [91], respectively. Ligands paths observed in dipolar aprotic solvents were attributed to reduction of the effective steric blocking by preferential solvation of the alkyl groups [93].

Palmer and Kelm [94], however, recently demonstrated that the absence of the ligand path is only true at low concentrations of incoming group. By working at higher nucleophile concentrations than were previously used, they showed that a two-term rate law applies for the reactions of $Pd(Et_4dien)X^+$ in water, with a reactivity order for incoming groups $S_2O_3^{2-} > SCN^- > N_3^- > Br^- \sim I^-$. The relative nucleophilicity order differs from the n°_{Pt} series which applies to unhindered complexes, specifically in the low reactivity of iodide, and in the almost equal reactivity of azide and thiocyanate. This demonstrates that size effects are important, but by no means exclusively so. The values of k_1 were constant for a given complex, and the activation parameters are in keeping with those expected for an associative mechanism [95,96]. The activation energy was negative for all the complexes studied [94] except for $Pd(Et_4dien)(NCS)^+$ where the value obtained was incompatible with previous results [97], but the early study seems to have neglected the effect of the reverse reaction. A k_2 path has also been reported for the reactions of $Pd(Et_4dien)Cl^+$ with NO_2^- and N_3^- in methanol [98].

Roulet and Gray [99] studied the activation parameters for the reactions of $Pd(Et_4dien)X^+$ with Y (X,Y = halide) in various solvents. In protic media the reactivity decreases in the order $X = Cl^- > Br^- > I^-$ with the activation enthalpy being the dominant factor. The activation entropy is negative and insensitive to the nature of X. Solvation and dissociation of the leaving group are thus of less importance than association of the complex with a solvent molecule to form a Pd—solvent bond. Proton NMR spectra show that solvation in the ground state decreases in the order $H_2O > CH_3OH > C_2H_5OH \sim DMSO \sim CH_2Cl_2$. Since the ground state is less solvated as the size of the solvent molecule increases, attainment of the transition state should require a greater measure of activation energy, as well as increased ordering in the system. For the protic solvents these expectations materialise in the observation of increasing values of $\Delta H_1^{\ddagger}$ and progressively more negative values of $\Delta S_1^{\ddagger}$, as the size of the solvent molecule increases.

In DMF and DMSO, however, the reactivity of $Pd(Et_4dien)X^+$ changes in the reverse order, namely, $X = I^- > Br^- > Cl^-$, which parallels the order of stability of these compounds. Similar observations were previously made for reactions in CH_3CN solution [92]. The activation entropies were considerably greater (more positive) than for protic solvents in which the extent of ground state solvation is similar [99]. This was interpreted as reflecting the operation of an I_d mechanism in the aprotic solvents in which leaving group solvation plays an important role. The mechanism was represented



$$\begin{tikzcd}
(\mathrm{Et_4dien})\mathrm{Pd{-}X} + \mathrm{S} \arrow[r, "\text{slow}"] & {[(\mathrm{Et_4dien})\mathrm{Pd} \cdots \mathrm{X}^-] \cdots \mathrm{S}} \arrow[d, "\text{fast}"] \\
& (\mathrm{Et_4dien})\mathrm{Pd{-}S} + \mathrm{X}^-
\end{tikzcd}$$

The reaction profile in this case would resemble Fig. 1(a), in which the bond-

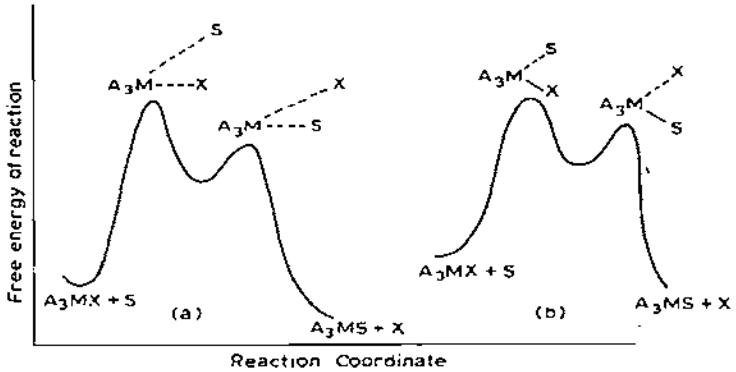
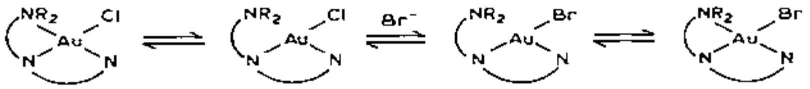


Fig. 1. Reaction profile for the reaction $MA_3X + S \rightarrow MA_3S + X$. (a) Bond breaking determines kinetics. (b) Associative solvolytic path. Very little bond breaking develops in transition state.

breaking step is the important stage, rather than Fig. 1(b) for the more usual solvolytic mechanism.

It should, however, be noted that the arguments presented rely on comparison of values of $\Delta S^{\ddagger}$ for which the error limits are inherently large. Moreover, while the results discussed above are satisfactorily interpreted in terms of a mechanism involving a greater extent of dissociation than usual, they fall short of providing unequivocal evidence for the participation of a three-coordinate intermediate derived from a "purely dissociative" step. A promising line of approach for these systems would appear to be the measurement of volumes of activation. Palmer and Kelm [100] have recently shown that $\Delta V_1^{\ddagger}$ for reactions of Pd(dien)X⁺ (X = halide) are significantly more negative than $\Delta V_2^{\ddagger}$ for the ligand path, and that $\Delta V_1^{\ddagger}$ is pressure dependent whereas $\Delta V_2^{\ddagger}$ is not. While these data can be explained by assuming a dissociative mechanism for the k_1 path, the picture is not unambiguous. Volume of activation studies on the $Pd(Et_4dien)X^+$ system may well help to clear up these problems as well as provide support for the solvent-assisted dissociation suggested by Roulet and Gray [99].

Dien complexes of gold(III) are fairly strong acids that yield conjugate base species $Au(dien\text{-}H)X^+$ at low pH. The reactions of these amido complexes are strongly influenced by the presence in the ligand of bulky alkyl groups, but the reactions are more complex than those of the palladium(II) complexes, and have been less systematically studied [59,101—103]. The unsubstituted compound $Au(dien\text{-}H)Cl^+$ was found to react with bromide almost exclusively by a ligand path [59,101]. On the other hand, Peshchevitskii and Shamovskaya reported that $Au(dien\text{-}H)Cl^+$ reacts with various ligands by a two-term rate law, but the ligand-independent term varied with the nature of the ligand by a factor of about twenty [103]. For the tetraethyl derivative $Au(Et_4dien\text{-}H)Cl^+$, the reaction was slower by some four orders of magnitude, and was almost independent of the nature and concentration of the incoming ligand [101]. The small ligand-dependent rate path was attributed to the intervention of a ring-opening mechanism of the type



Studies on a series of complexes with increasing alkyl substitution support this mechanism [102]. The coordinate nature of the ring-opened intermediates was not elaborated. Ring opening has also been postulated in the solvolysis reaction of Pd(dien)$(NH_3)^{2+}$ and in its reaction with chloride [104].

(ii) Bis(tertiary phosphine) complexes

The influence of bulky substituents on the phenyl ring in complexes of the type $Pt(PEt_3)_2RCl$ (R = phenyl, *o*-tolyl, mesityl) has been studied extensively [10,105—107]. Faraone et al. [106,107] found that methyl substituents in the *ortho* positions of the phenyl ring rendered the ligand path progressively less important, except for very powerful nucleophiles such as cyanide and thiourea. Further similarity with the pseudo-octahedral complexes of alkyl substituted dien was noted in that the ligand-independent rate constant was greater in methanol than in DMSO. This inversion of the usual order of solvent reactivity [86,108,109] was interpreted as evidence of relatively greater importance of bond breaking between the metal atom and the leaving group in the transition state. This resembles the discussion later supported by Roulet and Gray [99] for reactions of Pd(Et_4dien)X^+ in various solvents, and differs from the original suggestion that the size of the solvent molecule is the determining factor [92].

However, the most convincing evidence to date for the operation of a D mechanism, rather than an interchange scheme with strong dissociative component (I_d) comes not from substitution reactions, but rather from *cis* ⇌ *trans* isomerisation studies. Reactions of square-planar complexes are overwhelmingly stereospecific, and *cis* ⇌ *trans* isomerisation is usually a catalysed process, for which the three postulated mechanisms have been reviewed [110]. *cis*-$Pt(PEt_3)_2$(*o*-tolyl)Cl was the first compound found to undergo spontaneous uncatalysed isomerisation to the *trans* isomer [111]. The reaction was found to be subject to mass action retardation by chloride ion and is governed by a rate law of the form $k_{obs} = a/(b[Cl^-] + c)$. If a solvolytic pathway operates, the mechanism could be formulated as

$$\textit{cis}\text{-}Pt(PEt_3)_2(tol)Cl + S \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} \textit{cis}\text{-}Pt(PEt_3)_2(tol)S^+ + Cl^-$$

$$\textit{cis}\text{-}Pt(PEt_3)_2(tol)(S)^+ \xrightarrow{k_t'} \textit{trans}\text{-}Pt(PEt_3)_2(tol)(S)^+$$

$$\textit{trans}\text{-}Pt(PEt_3)_2(tol)(S)^+ + Cl^- \xrightarrow{\text{fast}} \textit{trans}\text{-}Pt(PEt_3)_2(tol)Cl + S$$

The rate equation governing the isomerisation would be $k_{obs}^{isom} = k_t'k_s/(k_{-s}[Cl^-] + k_t')$. In the absence of added chloride ion, this expression reduces to $k_{obs}^{isom} = k_s$, requiring the rate of unretarded isomerisation to be identical to the rate of solvolysis in the solvent path applicable to substitution reactions of the complex. The rate of isomerisation was, however, found to be slower by two orders of magnitude than the solvent path. Furthermore, the activation parameters for isomerisation differ considerably from those for the solvent path: the activation enthalpy for isomerisation is considerably greater than for solvolysis ($\Delta H_{isom}^{\ddagger} = 28.7$ kcal mol^{-1}: $\Delta H_s^{\ddagger} = 9.7$ kcal mol^{-1} in MeOH) while the activation entropy is strongly positive ($\Delta S_{isom}^{\ddagger} = 21$ cal K^{-1} mol^{-1}: $\Delta S_s^{\ddagger} = -32.5$ cal K^{-1} mol^{-1}). This is in marked contrast to the well documented negative values of $\Delta S^{\ddagger}$ characteristic of associative substitution processes [95,96].

The following mechanism was suggested to account for the observed kinetics (L = PEt_3; R = aryl ligand)

$$cis\text{-}PtL_2RCl \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \text{“}cis\text{”-}PtL_2R + Cl^-$$

$$\text{“}cis\text{”-}PtL_2R \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} \text{“}trans\text{”-}PtL_2R$$

$$\text{“}trans\text{”-}PtL_2R + Cl^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} trans\text{-}PtL_2RCl$$

As the isomerisation equilibrium lies well to the *trans* compound, k_{-t} and k_{-3} are negligible, and the following rate law may be derived, $k_{obs}^{isom} = k_dk_t/(k_{-d}[Cl^-] + k_t)$, which reduces to $k_{obs}^{isom} = k_d$ in the absence of mass-law retardation. Identity of k_{obs}^{isom} and k_s in the absence of added chloride is thus not to be expected. The reaction profile for isomerisation would thus contain three activated complexes as shown in Fig. 2.

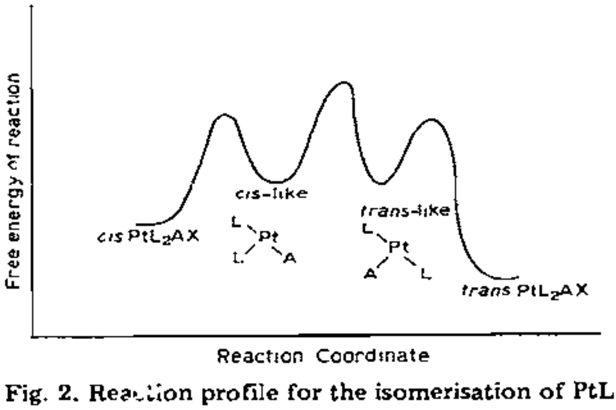
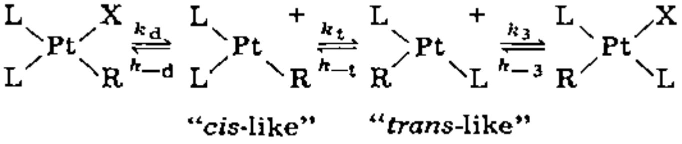


Fig. 2. Reaction profile for the isomerisation of PtL_2AX by a dissociative mechanism.

This study has been extended to other aryl groups and halides, and the results obtained [112,113] support the suggested rate-determining bond cleavage. Electron donating substituents on the aromatic nucleus enhance the rate of isomerisation in the order p-CH_3 > H > p-F, suggestive of stabilisation of the three coordinate intermediate(s) by charge neutralisation. The sequence of lability Cl > Br > I parallels the anticipated bond strength of the halide ions to the "soft" metal centre. Whereas bulky ortho substituents drastically reduce the rate of nucleophilic substitution in keeping with the associative (ligand or solvent) mechanism, such substitution has virtually no influence on the value of k_{isom}. For R = mesityl, X = Br, the rates of the solvolytic substitution path and of isomerisation are identical, as indeed are the activation parameters. Both reactions for this highly hindered molecule proceed by the same route, which is suggested to be the dissociative pathway. It should be noted, however, that the activation parameters for the mesityl compound more closely resemble those of the solvolysis path than those of the isomerisation mechanism for the complexes that do show both reactions.

Analogous compounds where R = CH_3, C_2H_5 have been shown to isomerise spontaneously in protic solvents and obey the same form of kinetic equation, with k_{obs}^{isom} considerably smaller than the rate of the solvolytic substitution path [114]. The presence of an aromatic group is thus not a prerequisite for the dissociative isomerisation mechanism.

A T-shaped structure, either "*cis*-like" or "*trans*-like" (see (17) below), has been suggested for the three-coordinate intermediates of the dissociative path, in which the geometry of the original complex is essentially retained [111—114]. If a trigonal planar intermediate were involved, bond-angle opening would be expected to be reflected in increased rates of reaction as the steric requirements of the complex are increased. As noted above, the values of k_{isom} are essentially insensitive to the presence of bulky substituents close to the site of reaction. The mechanism may thus be explicitly summarised as follows



(17)

where in most cases k_{-3} and k_{-t} are negligible and the equilibrium position lies well to the *trans* side.

(iii) Other complexes

Evidence for three-coordinate intermediates has been obtained from a variety of migration reactions. Hydride complexes of the type *trans*-$PtL_2(H)X$ undergo insertion of olefins into the metal hydride bond yielding alkyl complexes [115—117].

trans-$PtL_2(H)X$ + ol → *trans*-PtL_2(alkyl)X

When L = PEt_3, vigorous conditions are required if X = Cl^-; but when X is an easily displaced ligand such as NO_3^- or acetone the reaction is facile [115—117]. The first step of the postulated mechanism is rapid formation of an olefin hydride complex. Such species have been isolated [115].

$$\textit{trans}\text{-PtL}_2\text{(H)X} + \text{ol} \rightarrow \textit{trans}\text{-PtL}_2\text{(ol)(H)}^+ + \text{X}^-$$

(I)

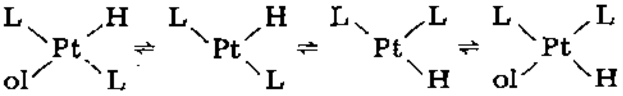
Two alternative mechanisms have been suggested for the subsequent stages: a five coordinate intermediate is formed by interaction between (I) and another molecule or olefin or by the displaced group X [118]. However, for the reaction of *trans*-$Pt(PEt_3)_2(H)(NO_3)$ with methylacrylate, a three-coordinate intermediate was suggested [119].

$$\textit{trans}\text{-PtL}_2\text{(H)(NO}_3\text{)} + \text{ol} \rightleftharpoons \textit{trans}\text{-PtL}_2\text{(H)(ol)} + \text{NO}_3^-$$

$$\textit{trans}\text{-PtL}_2\text{(H)(ol)} \rightleftharpoons \textit{cis}\text{-PtL}_2\text{(H)(ol)}$$

$$\textit{cis}\text{-PtL}_2\text{(H)(ol)} \xrightarrow{\text{slow}} \text{“PtL}_2\text{R”} \overset{\text{fast}}{\rightleftharpoons} \textit{trans}\text{-PtL}_2\text{R(NO}_3\text{)}$$

The dependence of the rate on the concentration of methylacrylate is of the form $k_{obs} = a[\text{ol}]/(b[\text{ol}] + c)$, as expected for the fast pre-equilibrium between the complex and olefin. Mass-law retardation by nitrate is also observed. The hydride and olefin ligands must occupy *cis* positions for migration to occur. Romeo et al. [114] suggested that since the olefin is coordinated *trans* to the highly labilising hydride ligand, it may dissociate to a sufficient extent to allow the mechanism discussed in the previous section to operate.



(II)

Subsequent proton migration yields the three-coordinate alkyl intermediate "PtL_2R", although attack by olefin on the *cis*-like intermediate (II) may yield the alkyl group directly.

The action of various ligands on carbonyl alkyl complexes can cause the insertion of carbon monoxide into the metal—alkyl bond [120], e.g.

$$\text{Pt(AsPh}_3\text{)(CO)(C}_2\text{H}_5\text{)Cl} + \text{AsPh}_3 \rightarrow \text{Pt(AsPh}_3\text{)}_2\text{(COC}_2\text{H}_5\text{)Cl}$$

For this reaction plots of $1/k_{obs}$ against $1/[AsPh_3]$ were found to be linear in diethylketone, cyclohexanone, THF and chlorobenzene, but the rate was independent of ligand concentration in 1,2 dichloroethane and nitrobenzene. This is in accordance with the following mechanism

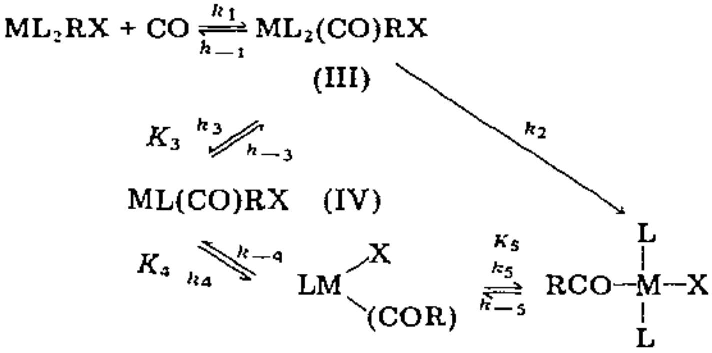
$$\text{Pt(AsPh}_3\text{)(CO)(C}_2\text{H}_5\text{)Cl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Pt(AsPh}_3\text{)(COC}_2\text{H}_5\text{)Cl}$$

$$Pt(AsPh_3)(COC_2H_5)Cl + AsPh_3 \xrightarrow{k_2} Pt(AsPh_3)_2(COC_2H_5)Cl$$

for which the rate law is $k_{obs} = k_1k_2[AsPh_3]/(k_{-1} + k_2[AsPh_3])$.

In those solvents in which $k_2[AsPh_3] >> k_{-1}$, this expression reduces to $k_{obs} = k_1$. This mechanism is kinetically indistinguishable from one in which the reversible first step is the familiar solvolytic formation of a four-coordinate solvento complex. This alternative was discounted because the value of k_1 was found to decrease with the coordinating ability of the solvent, while the activation entropy was considerably greater than expected for solvent assisted carbonyl insertion. The mechanism requires k_1 to be independent of the nature of the attacking ligand, and for a number of incoming groups almost identical values of k_1 were obtained [121].

Garrou and Heck [122] studied the formation of alkoyl complexes by the action of carbon monoxide on alkyl complexes, and suggested the following comprehensive mechanism for the reaction of ML_2RX (M = Ni, Pd, Pt; L = tertiary phosphine)

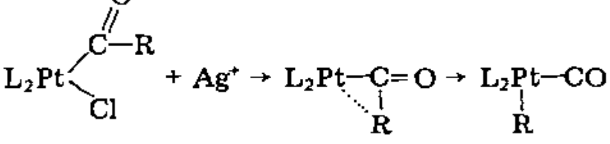


The existence of a five-coordinate intermediate (III) was supported by IR and NMR evidence, and in one instance the intermediate was isolated. Rearrangement of (III) to the alkoyl product may be direct (k_2) or may be preceded by the loss of a phosphine molecule in the k_3 path. Rearrangement of (IV) gives a three-coordinate alkoxy intermediate which gives the final product by readdition of phosphine. As expected, the path via k_3, k_4, k_5 exhibits mass-law retardation by phosphine.

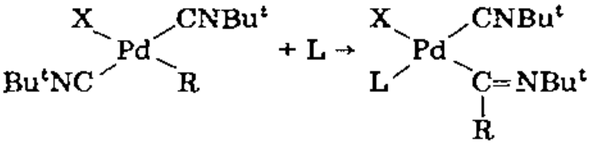
The formation of alkyl carbonyl complexes by the reaction

$$PtL_2(RCO)Cl \rightarrow PtL_2(CO)R^+ + Cl^-$$

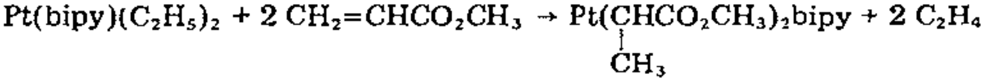
can be regarded as the reverse of the migration reaction. In ethanol solution, silver ions catalyse this reaction, and an approximately three-coordinate intermediate has been suggested to participate ($L = PPh_3$).



In the better coordinating solvent, acetonitrile, silver ions simply displace chloride yielding the solvento complex, $PtL_2(RCO)(CH_3CN)^+$ [123]. Another migration reaction in which three-coordinate intermediates may participate (although kinetic studies were not sufficiently encompassing to exclude other possibilities) is rearrangement of the bis(isocyanide) complex $Pd(CNBu^t)_2XR$ under the influence of various groups L [124].

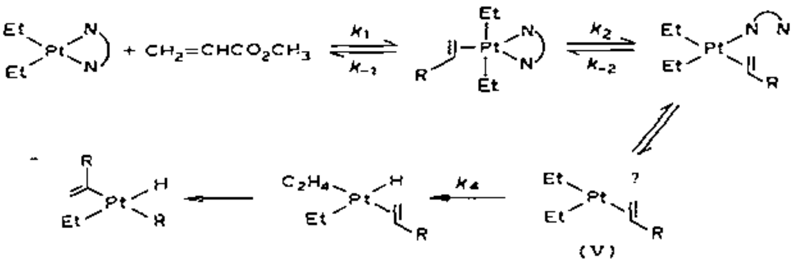


In the reaction of $Pt(bipy)(C_2H_5)_2$ with methylacrylate, ethylene is eliminated [125].



$$Pt(bipy)(C_2H_5)_2 + 2\ CH_2{=}CHCO_2CH_3 \rightarrow Pt(\underset{CH_3}{\underset{|}{C}}HCO_2CH_3)_2bipy + 2\ C_2H_4$$

Since none of the ligands initially present is easily displaced, the first step must be associative, and the rate is first order in olefin. The reaction rate is retarded by free bipy, which can be shown independently not to react with either the starting material or the product of the reaction. The following mechanism was suggested, where the role of added bipy can be seen to retard formation of subsequent intermediates. Formation of (V) with a (presumably) vacant coordination site is necessary for β-elimination and hydride formation. Ethylene is then quickly replaced by methylacrylate followed by insertion of the ligand into the metal hydride bond. These steps are repeated for formation of the second metal—carbon σ bond, and finally bipyridyl replaces the π-bonded methylacrylate. All steps subsequent to k_4 are presumed to be fast, and the mechanism is compatible with (V) being three-coordinate. Again, the kinetic studies are not comprehensive enough to verify this point (nor indeed was this the main aim of the study).



Dissociative intermediates have been suggested for the reactions of Au-$(PPh_3)(t\text{-}Bu)(CH_3)_2$ [126]. Depending on the reaction conditions three reactions may occur (19).

$$\mathrm{Au(PPh_3)(t\text{-}Bu)Me_2}\left\{\begin{array}{l}\xrightarrow[\text{alkyl group}]{\text{(a) isomerisation of}} \mathrm{Au(PPh_3)(i\text{-}Bu)Me_2} \\ \xrightarrow[\text{isomerisation}]{\text{(b) } cis\text{-}trans} \mathrm{Au(PPh_3)(t\text{-}Bu)Me_2} \\ \xrightarrow[\text{elimination}]{\text{(c) reductive}} \mathrm{Au(PPh_3)R}\end{array}\right. \qquad (19)$$

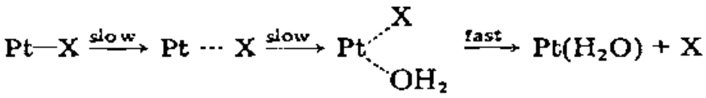
The rates of (a) and (c) are retarded by added phosphine, suggesting a possible mechanism involving the intermediate $AuRMe_2$. This species undergoes β-elimination and readdition across a different CH bond in the isomerisation path (a), or loss of 2 alkyl groups and readdition of phosphine in the reductive elimination option. The activation parameters for the isomerisation of the butyl group ($\Delta H^{\ddagger} = 29$ kcal mol^{-1}; $\Delta S^{\ddagger} = 16$ cal K^{-1} mol^{-1}) are in keeping with a dissociative mechanism: however, neither this nor the necessity for a "vacant" coordination site to facilitate β-elimination excludes the possible involvement of four-coordinate solvento intermediates. *Cis* $\rightleftharpoons$ *trans* isomerisation is not influenced by added phosphine and the unusual mechanism of spontaneous interconversion via a tetrahedral transition state was suggested.

(iv) Mixed solvents

Frequently conclusions regarding the mechanism of the k_1 path of substitution reactions have been sought from the behaviour of this term in different solvents. In most studies involving pure solvents the results were interpreted in terms of the associative model as discussed above, but some authors have viewed these changes as reflecting a dissociative model. Thus a dissociative k_1 path was inferred for the exchange of labelled acetylacetonate with $Pd(acac)_2$ because of the correlation of the rate constant with the dielectric constant (charge separating ability) of the solvent [127]. However, the variation of rate as a function of solvent properties has been most systematically studied in mixed solvents. Panasyak et al. studied the rates of hydrolysis and substitution reactions of platinum and palladium complexes in mixed aqueous organic solvents [128—132]. The rate of hydrolysis of $Pt(en)Cl_2$ and *cis*-$Pt(NH_3)_2Cl_2$ in aqueous methanol, ethanol and acetone falls in all cases as the organic content is increased. The results were interpreted in terms of Kirkwood's equation from transition state theory

$$\log k = \log k_0 - \frac{1}{KT}\left(\frac{D-1}{2D+1}\right)\left(\frac{\mu_a^2}{r_a^3} - \frac{\mu_\pm^2}{r_\pm^3}\right)$$

where D is the dielectric constant of the medium, and μ and r are the dipole moment and radius respectively of the ground state, a, and the transition state, ±, respectively. Plots of log k against the dielectric constant function denoted $f(D)$, were found to be linear but each solvent system was described by a separate line. In all cases the slopes were markedly greater than for the bimolecular reaction between NH_3 and *trans*-$Pt(NH_3)_2Cl_2$. This eliminates the possibility of a pure S_N2 hydrolysis mechanism. Similarly, a limiting S_N1 mechanism was ruled out because of the absence of correlation of log *k* with the square root of the ionic strength. The data were interpreted in terms of non-limiting S_N1 two-stage activation, represented schematically.



$$\mathrm{Pt{-}X} \xrightarrow{\text{slow}} \mathrm{Pt \cdots X} \xrightarrow{\text{slow}} \mathrm{Pt}\begin{smallmatrix}\cdot\cdot\mathrm{X}\\ \cdot\cdot\mathrm{OH_2}\end{smallmatrix} \xrightarrow{\text{fast}} \mathrm{Pt(H_2O) + X}$$

This corresponds to an I_d mechanism with reaction profile similar to that represented in Fig. 1a. Similar results were obtained, and a similar I_d mechanism suggested for the hydrolysis of Pt(acetoxime)Cl_2 in aqueous organic media [131]. However, this promising line of approach was shown to be extremely limited, when an attempt was made to extend the treatment to the hydrolysis of *trans*[$Pd(NH_3)_2XY$] (X = Y = Cl^- or NO_2^-; X = Cl^-; Y = NO_2^- or H_2O) in aqueous methanol, acetone, dioxan and DMF [130]. For each solvent a different straight line was obtained when log *k* was plotted against *f*(*D*), and more important, the direction of variation of log *k* with *f*(*D*) was irregular. Thus the following changes were noted

Mixed solvent	H_2O CH_3OH	H_2O DMF	H_2O dioxan	H_2O acetone
Hydrolysis of				
$Pd(NH_3)_2Cl_2$	decrease	decrease	increase	increase
$Pd(NH_3)_2(NO_2)Cl$	decrease	increase	increase	increase
$Pd(NH_3)_2(NO_2)(H_2O)^+$	increase	—	increase	decrease

It is not clear how these results may be rationalised, but the limited predictive power of the technique is apparent.

Recently, an attempt has been made to correlate rate constants in mixed solvents with the Grunwald—Winstein *Y* parameter [133]. The problem that arises here is the interpretation of the different values of slopes of plots of log *k* against *Y*. The definition of *Y* with respect to the specific organic reaction uses as reference a reaction system of vastly different properties from those of transition metal complexes. The reactions of Pd(dien)X^+ (X = Cl, Br) with various nucleophiles were suggested as suitable inorganic models for an S_N2 mechanism, and the hydrolysis of Pt(Et_4dien)X^+ as a prototype solvent-assisted dissociative mechanism. The data of Panasyuk and Malashok [129] were interpreted in terms of the *Y* parameter. It was suggested that for the solvolysis reactions of Pt(en)Cl_2 and *cis*-$Pt(NH_3)_2Cl_2$ as well as for the hydrolysis reactions of Pd(dien)I^+ and Pd(Et_4dien)I^+, a reaction profile applies in which bond breaking determines the activation energy, whereas for the reaction of NH_3 with *trans*-$Pt(NH_3)_2Cl_2$ bond formation is decisive in keeping with the classic associative picture.

D. CONCLUSIONS

It can be seen that the frequently quoted two-path associative mechanism (3) is in many cases an approximate description of a considerably more complex picture. Detailed kinetic studies of substitution reactions, particularly with regard to the concentration dependence of the leaving group, are essential for a full appreciation of the role of the solvent. Even where this is done differentiation between associative solvent attack and dissociation of the substrate has been unequivocally demonstrated only for *cis* ⇌ *trans* isomerisation. Evidence for the dissociative mechanism in most other cases is to date circumstantial. The search for other reaction systems involving three-coordinate intermediates appears to offer a fruitful field of activity.

REFERENCES

1 F. Basolo and R.G. Pearson, Mechanism of Inorganic Reactions, 2nd Ed., Wiley, New York, 1967, chap. 5.
2 C.H. Langford and H.B. Gray, Ligand Substitution Processes, Benjamin, New York, 1966, chap. 2.
3 (a) L. Cattalini, Prog. Inorg. Chem., 13 (1970) 263. (b) L. Cattalini, in M.L. Tobe (Ed.), MTP International Review of Science, Inorganic Chemistry, Series One, Vol. 9, Reaction Mechanism in Inorganic Chemistry, p. 269.
4 M.L. Tobe, Inorganic Reaction Mechanisms, Nelson, London, 1972, chap. 5.
5 R.G. Wilkins, The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes, Allen and Bacon, Boston, 1974, chap. 4.
6 L. Cattalini, R. Ugo and A. Orio, J. Am. Chem. Soc., 90 (1968) 4800.
7 A.J. Hall and D.P.N. Satchell, J. Chem. Soc. Chem. Commun., (1976) 163.
8 J.-Y. Seguin, P.-C. Kong and M. Zador, Can. J. Chem., 52 (1974) 2603.
9 J.-Y. Seguin and M. Zador, Inorg. Chim. Acta, 20 (1976) 203.
10 V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. Dalton, (1972) 1857.
11 G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. Dalton, (1974) 1377.
12 V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. Dalton, (1974) 927.
13 F. Basolo, J. Chatt, H.B. Gray, R.G. Pearson and B.L. Shaw, J. Chem. Soc., (1961) 2207.
14 P. Pietropaolo, P. Uguagliati, M. Graziani and U. Belluco, Inorg. Chim. Acta, 4 (1970) 637.
15 J. Hubert and T. Theophanides, Inorg. Chim. Acta, 3 (1969) 391.
16 R. Pietropaolo, F. Faraone, D. Pietropaolo and P. Piraino, J. Inorg. Nucl. Chem., 36 (1974) 369.
17 P. Uguagliati, U. Belluco, U. Croatto and R. Pietropaolo, J. Am. Chem. Soc., 89 (1967) 1336.
18 J.E. Teggins, K.W. Lee, J.M. Baker and E.D. Smith, J. Coord. Chem., 1 (1971) 215.
19 R.G. Pearson and D.A. Johnson, J. Am. Chem. Soc., 86 (1964) 3983.
20 R.A. Reinhardt and W.W. Monk, Inorg. Chem., 9 (1970) 2026.
21 A.J. Poë and D.H. Vaughan, Inorg. Chim. Acta, 1 (1967) 255.
22 G. Carturan and D.S. Martin, Inorg. Chem., 9 (1970) 258.
23 J.E. Teggins, J.A. McCann and E.D. Smith, Inorg. Chem., 9 (1970) 1294.
24 R.C. Conrad and J.V. Rund, Inorg. Chem., 11 (1972) 129.
25 D.E. Schwab and J.V. Rund, Inorg. Chem., 11 (1970) 499.
26 F. Aprile and D.S. Martin, Inorg. Chem., 1 (1962) 551.

27 W.H. Jolly, E.D. Smith, D.S. Martin, J.C. Clardy and J.D. Woods, Inorg. Chem., 11 (1972) 2866.
28 V.D. Panasyuk and N.F. Malashok, Russ. J. Inorg. Chem., 13 (1968) 1405.
29 D.S. Martin, Inorg. Chim. Acta Rev., 1 (1967) 87.
30 D. Banerjea, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 79 (1957) 4055.
31 L. Cattalini, M. Nicolini and A. Orio, Inorg. Chem., 5 (1966) 1674.
32 J.S. Coe and J.R. Lyons, J. Chem. Soc. (A), (1969) 2669.
33 H.B. Gray and R.J. Olcott, Inorg. Chem., 1 (1962) 481.
34 P. van Z. Bekker and W. Robb, Int. J. Chem. Kin., 7 (1975) 87.
35 C.G. Nicholson and W. Robb, Inorg. Chim. Acta, 8 (1974) 41.
36 R.J. Mureinik and M. Bidani, unpublished results.
37 F.A. Palocsay and J.V. Rund, Inorg. Chem., 8 (1969) 524.
38 J.V. Rund, Inorg. Chem., 9 (1970) 1211.
39 W.R. Mason, Inorg. Chem., 9 (1970) 2688.
40 L. Cattalini, A. Orio and M. Nicolini, J. Am. Chem. Soc., 88 (1966) 5734.
41 L. Cattalini, A. Orio and M.L. Tobe, J. Am. Chem. Soc., 89 (1967) 3130.
42 V.A. Golvnya and I.V. Prokof'eva, Izv. Sektora Platiny, USSR, 27 (1952) 62; Chem. Abstr., 50 (1956) 1652d.
43 L.I. Elding, Inorg. Chim. Acta, 6 (1972) 683.
44 R.J. Mureinik, Inorg. Chim. Acta, 13 (1975) 127.
45 L.I. Elding, Acta Chem. Scand., 20 (1966) 2559.
46 L. Drougge, L.I. Elding and L. Gustafson, Acta Chem. Scand., 21 (1967) 1647.
47 L.I. Elding, Acta Chem. Scand., 24 (1970) 1527.
48 R.M. Milburn and R.M. Venanzi, Inorg. Chim. Acta, 2 (1968) 97.
49 M. Green and C.J. Wilson, Discus. Faraday Soc., 47 (1969) 111.
50 J.E. Teggins and T.S. Woods, Inorg. Chem., 7 (1968) 1424.
51 R.J. Mureinik, J. Chem. Soc. Dalton, (1976) 1036.
52 C.B. Colvin, R.G. Gunther, L.D. Hunter, J.A. McLean, M.A. Tucker and D.S. Martin, Inorg. Chim. Acta, 2 (1968) 487.
53 W. Robb and C.G. Nicholson, Inorg. Chim. Acta, 7 (1973) 645.
54 R.G. Collins and D.A. Johnson, J. Inorg. Nucl. Chem., 33 (1971) 1861.
55 V.A. Valyaeva, Russ. J. Inorg. Chem., 20 (1975) 1507.
56 J.V. Rund and F.A. Palocsay, Inorg. Chem., 8 (1969) 2242.
57 J.H. Cawley and J.V. Rund, J. Inorg. Nucl. Chem., 32 (1970) 1406.
58 J.V. Rund, Inorg. Chem., 13 (1974) 738.
59 F. Basolo and W.H. Baddley, Inorg. Chem., 3 (1964) 1087.
60 W. Robb and R.J. Mureinik, Inorg. Chim. Acta, 3 (1969) 575.
61 R.J. Mureinik and W. Robb, Inorg. Chim. Acta, 3 (1969) 580.
62 L. Baracco, L. Cattalini, J.S. Coe and E. Rotondo, J. Chem. Soc. (A), (1971) 1517.
63 Yu.N. Kukushkin and V.B. Ukraintsev, Russ. J. Inorg. Chem., 13 (1968) 1485.
64 Yu.N. Kukushkin and V.B. Ukraintsev, Russ. J. Inorg. Chem., 17 (1972) 1407.
65 L.F. Grantham, T.S. Elleman and D.S. Martin, J. Am. Chem. Soc., 77 (1955) 2965.
66 R.D. Gillard and J.R. Lyons, J. Chem. Soc. Chem. Commun., (1973) 546.
67 R.D. Gillard, Coord. Chem. Rev., 16 (1975) 67.
68 E. Bielli, R.D. Gillard and D.W. James, J. Chem. Soc. Dalton, (1976) 1837.
69 W.J. Louw and W. Robb, Inorg. Chim. Acta, 3 (1969) 29.
70 W.J. Louw and W. Robb, Inorg. Chim. Acta, 3 (1969) 303.
71 P. van Z. Bekker, W.J. Louw and W. Robb, Inorg. Chim. Acta, 6 (1972) 564.
72 W.J. Louw and W. Robb, Inorg. Chim. Acta, 8 (1974) 253.
73 D.J. de Waal and W. Robb, Int. J. Chem. Kin., 6 (1974) 309.
74 D.J. de Waal and W. Robb, Int. J. Chem. Kin., 6 (1974) 323.
75 P. van Z. Bekker and W. Robb, Inorg. Nucl. Chem. Lett., 8 (1972) 849.
76 R.M. Henry, J. Am. Chem. Soc., 86 (1964) 324.
77 P.M. Maitlis, The Organic Chemistry of Palladium, Acad. Press, N.Y., 1971.

78 R. Pietropaolo, P. Uguagliati, T. Boschi, B. Crociani and U. Belluco, J. Catalysis, 18 (1970) 338.
79 R. Pietropaolo, F. Faraone, S. Sergi and D. Pietropaolo, J. Organometal. Chem., 42 (1972) 177.
80 P. Pietropaolo, E. Rotondo, F. Faraone and D. Pietropaolo, J. Organometal. Chem. 60 (1973) 197.
81 H.C. Clark and W.J. Jacobs, Inorg. Chem., 9 (1970) 1229.
82 R.G. Pearson, H.B. Gray and F. Basolo, J. Am. Chem. Soc., 82 (1960) 787.
83 U. Belluco, P. Rigo, M. Graziani and R. Ettore, Inorg. Chem., 5 (1966) 1125.
84 U. Belluco, A. Orio and M. Martelli, Inorg. Chem., 5 (1966) 1370.
85 R.S. Drago, V.A. Mode and J.G. Kay, Inorg. Chem., 5 (1966) 2050.
86 U. Belluco, M. Graziani, M. Nicolini and P. Rigo, Inorg. Chem., 6 (1967) 721.
87 L. Cattalini, V. Ricevuto, A. Orio and M.L. Tobe, Inorg. Chem., 7 (1968) 51.
88 T.P. Cheeseman, A.L. Odell and H.A. Raethall, Chem. Commun., (1968) 1496.
89 S.S. Hupp and G. Dahlgren, Inorg. Chem., 15 (1976) 2349.
90 W.H. Baddley and F. Basolo, J. Am. Chem. Soc., 88 (1966) 2944.
91 J.B. Goddard and F. Basolo, Inorg. Chem., 7 (1968) 936.
92 J.B. Goddard and F. Basolo, Inorg. Chem., 7 (1968) 2456.
93 K.A. Johnson, J.C. Lim and J.L. Burmeister, Inorg. Chem., 12 (1973) 124.
94 D.A. Palmer and H. Kelm, Inorg. Chim. Acta, 14 (1975) L27.
95 U. Belluco, R. Ettore, F. Basolo, R.G. Pearson and A. Turco, Inorg. Chem., 5 (1966) 591.
96 R. Romeo, M.L. Tobe and M. Trozzi, Inorg. Chim. Acta, 11 (1974) 231.
97 F. Basolo, W.H. Baddley and K.J. Weidenbaum, J. Am. Chem. Soc., 88 (1966) 1576.
98 M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo and M. Trozzi, Inorg. Chim. Acta, 16 (1976) 135.
99 R. Roulet and H.B. Gray, Inorg. Chem., 11 (1972) 2101.
100 D.A. Palmer and H. Kelm, Inorg. Chim. Acta, 19 (1976) 117.
101 C.F. Weick and F. Basolo, Inorg. Chem., 5 (1966) 576.
102 D.L. Fant and C.F. Weick, Inorg. Chem., 12 (1973) 1864.
103 B.I. Peshchevitskii and G.I. Shamovskaya, Russ. J. Inorg. Chem., 17 (1972) 1386.
104 J.S. Coe and J.R. Lyons, J. Chem. Soc. (A), (1969) 2669.
105 U. Belluco, P. Rigo and M. Graziani, Inorg. Chem., 5 (1966) 1123.
106 G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, Inorg. Chem., 8 (1969) 2207.
107 G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, Inorg. Chem., 9 (1970) 1525.
108 C.H. Langford, Inorg. Chem., 3 (1964) 228.
109 U. Belluco, M. Martelli and A. Orio, Inorg. Chem., 5 (1966) 583.
110 R. Romeo, P. Uguagliati and U. Belluco, J. Mol. Catal., 1 (1976) 325.
111 G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. (A), (1971) 1877.
112 R. Romeo, D. Minniti and M. Trozzi, Inorg. Chim. Acta, 14 (1975) L15.
113 R. Romeo, D. Minniti and M. Trozzi, Inorg. Chem., 11 (1976) 1134.
114 R. Romeo, D. Minniti and S. Lanza, Inorg. Chim. Acta, 18 (1976) L15.
115 A.J. Deeming, B.F.G. Johnson and J. Lewis, Chem. Commun., (1970) 598.
116 H.C. Clark and H. Kurosawa, Inorg. Chem., 11 (1972) 1275.
117 H.C. Clark, C. Jablonski, J. Halpern, A. Mantanovi and T.A. Weil, Inorg. Chem., 13 (1974) 1541.
118 H.C. Clark and C.R. Jablonski, Inorg. Chem., 13 (1974) 2213.
119 H.C. Clark and C.S. Wong, J. Am. Chem. Soc., 96 (1974) 7213.
120 R.W. Glyde and R.J. Mawby, Inorg. Chem., 10 (1971) 854.
121 R.W. Glyde and R.J. Mawby, J. Chem. Soc. Dalton, (1974) 1293.
122 P.E. Garrou and R.F. Heck, J. Am. Chem. Soc., 98 (1976) 4115.
123 M. Kubota, R.K. Rothrock and J. Geibel, J. Chem. Soc. Dalton, (1973) 1267.
124 S. Otsuka and K. Ataka, J. Chem. Soc. Dalton, (1976) 327.

125 N. Chaudhury and R.J. Puddephatt, J. Chem. Soc. Dalton, (1976) 915.
126 A. Tamaki, S.A. Magennis and R.K. Kochi, J. Am. Chem. Soc., 96 (1974) 6140.
127 K. Saito and M. Takahashi, Bull. Chem. Soc. Jpn., 42 (1969) 3462.
128 V.D. Panasyuk and N.F. Malashok, Russ. J. Inorg. Chem., 14 (1969) 525.
129 V.D. Panasyuk and N.F. Malashok, Russ. J. Inorg. Chem., 14 (1969) 681.
130 V.D. Panasyuk and T.I. Denisova, Russ. J. Inorg. Chem., 15 (1970) 1422.
131 V.D. Panasyuk, N.F. Falendysh and N.A. D'yachenko, Russ. J. Inorg. Chem., 16 (1971) 1452.
132 V.D. Panasyuk, T.I. Denisova and S.K. Rybak, Russ. J. Inorg. Chem., 17 (1972) 874.
133 L.A.P. Kane-Maguire and G. Thomas, J. Chem. Soc. Dalton, (1975) 1890.