Studies on $[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$. Part 2.[1] Kinetic and Mechanistic Studies on the Reaction of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with 2,2′-Bipyridine or $Et_2PCH_2CH_2PEt_2$ at 25 °C

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The kinetics of the reactions between *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ and L–L = 2,2′-bipyridine or $Et_2PCH_2CH_2PEt_2$ to give *mer*-$[VCl_3(OPMe_2Ph)(L–L)]$ have been studied in tetrahydrofuran (thf) at 25 °C. Previous proposals that in solution the reactant is the solvento-species $[VCl_2(OPMe_2Ph)(PMe_2Ph)(thf)_2]^+$ have been substantiated by kinetic studies which demonstrate that chloride must bind to the reactant prior to interaction with the substrates. The kinetics has been interpreted in terms of a series of associative-interchange steps. Strong evidence for the associative mechanism comes from the observation that the solvento-species does not react with L–L, a pattern which is inconsistent with a dissociative mechanism.

There have been several studies on the exchange and substitution reactions of $[V(OH_2)_6]^{3+}$ which conclude that the mechanism is I_a. These proposals are based, in the main, on extra-kinetic parameters, primarily volumes of activation[2–4] ($\Delta V^{\ddagger} = -10$ cm^3 mol^{-1} for water exchange), and the value of the ratio for the rate constants for reaction with thiocyanate and chloride (k_{NCS}/k_{Cl}).[5] A major restricting factor in the kinetic analysis of the substitution reactions of $[V(OH_2)_6]^{3+}$ is the preponderance of water: present as the leaving group, entering group, spectator ligands and the solvent.

Herein is reported a kinetic study on the substitution reactions of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ in tetrahydrofuran (thf) as shown in equation (1), where L–L = 2,2′-

$$\textit{trans,mer}\text{-}[VCl_3(OPMe_2Ph)(PMe_2Ph)_2] + L–L \longrightarrow \textit{mer}\text{-}[VCl_3(OPMe_2Ph)(L–L)] + 2PMe_2Ph \quad (1)$$

bipyridine (bipy) or $Et_2PCH_2CH_2PEt_2$ (depe), which avoids the ambiguities of the aqua-system since the nucleophile, leaving group, coligands and solvent are all different.

In addition the reactant complex and the product (when L–L = depe) have been structurally characterised by X-ray crystallography, and their solution properties probed by EPR spectroscopy,[1] making this a good system to investigate the kinetics of substitution at an octahedral, fourteen-electron, vanadium(III) centre: a metal whose reactivity has been only poorly probed so far.

Results

The kinetics of the reactions between *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ and bipy or depe have been studied in thf using stopped-flow spectrophotometry. The analogous reaction with $Me_2NCH_2CH_2NMe_2$ has not been studied since in thf this reaction is very slow at 25.0 °C.

Kinetics with bipy.—At a constant concentration of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ (2.5×10^{-4} mol dm^{-3}) the reaction with bipy (2.5–50 mmol dm^{-3}) exhibits a single exponential absorbance–time curve, with an initial absorbance which is that of the parent complex and a final absorbance which is that of $[VCl_3(OPMe_2Ph)(bipy)]$ in thf. The kinetics of this reaction shows a simple first-order dependence on the concentration of the vanadium complex, but a complicated

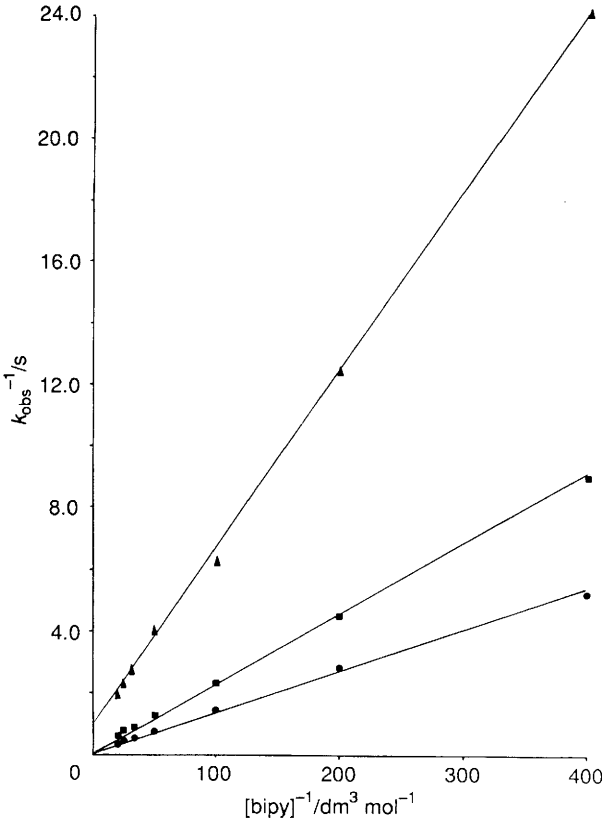


Fig. 1 Dependence of $1/k_{obs}$ on 1/[bipy] for the reaction of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with 2,2′-bipyridine at 25 °C in thf. The data shown are: in the absence of $[PBu_4]Cl$ (▲), line drawn is that defined by equation (2); in the presence of $[PBu_4]Cl$, $[Cl^-] = 2.0$ (■) or 10.0 mmol dm^{-3} (●), lines drawn are those defined by equation (3)

dependence on the concentration of bipy as shown by the data in Table 1. Thus as the concentration of bipy increases from 2.5 to 50 mmol dm^{-3} the dependence of the reaction rate on the concentration of bipy changes from first to zero order. Analysis of these data by the normal double-reciprocal plot[6] shown in Fig. 1 allows the derivation of the rate equation (2). This kinetics is unperturbed by the addition of an excess of PMe_2Ph (1–20

Table 1 Kinetic data for the reaction of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with bipy at 25.0 °C in thf (λ = 420 nm, [V] = 2.5 × 10^{-4} mol dm^{-3})

[bipy]/mmol dm^{-3}	$[Cl^-]$*/mmol dm^{-3}	k_{obs}/s^{-1}
2.5		0.04
5.0		0.08
10.0		0.16
20.0		0.25
30.0		0.37
40.0		0.43
50.0		0.48
2.5	2.0	0.11
5.0		0.20
10.0		0.43
20.0		0.80
30.0		1.18
40.0		1.33
50.0		1.65
2.5	10.0	0.19
5.0		0.35
10.0		0.71
20.0		1.25
30.0		2.00
40.0		2.00
50.0		2.52
5.0	1.0	0.16
	2.0	0.23
	4.0	0.29
	7.0	0.32
	10.0	0.36
10.0	1.0	0.30
	2.0	0.43
	4.0	0.58
	7.0	0.69
	10.0	0.71
40.0	1.0	0.91
	2.0	1.43
	4.0	1.92
	7.0	2.22
	10.0	2.86

* Supplied as $[PBu_4]Cl$.

Table 2 Kinetic data for the reaction of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with depe at 25.0 °C in thf (λ = 400 nm, [V] = 5 × 10^{-4} mol dm^{-3})

[bipy]/mmol dm^{-3}	$[Cl^-]$*/mmol dm^{-3}	k_{obs}/s^{-1}
5.0		0.9
10.0		1.1
20.0		1.0
50.0		1.1
5.0	2.5	6.8
	5.0	13.5
	10.0	28.0
	20.0	60.0

* Supplied as $[PBu_4]Cl$.

$$k_{obs} = \frac{(17.2 \pm 0.3)[bipy]}{1 + (19.0 \pm 0.2)[bipy]} \quad (2)$$

mmol dm^{-3}), but markedly affected by the introduction of chloride (as $[PBu_4]Cl$) into the system, as shown by the data in Table 1 and illustrated in Figs. 1 and 2.

Analysis of the kinetics of the reaction in the presence of chloride is complicated since it proved impossible to dissect graphically the dependence on the concentration of chloride

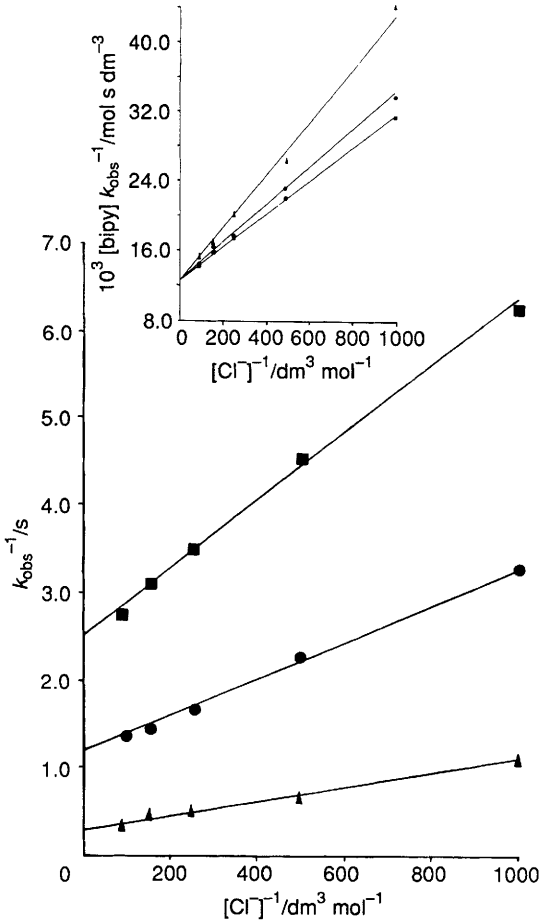


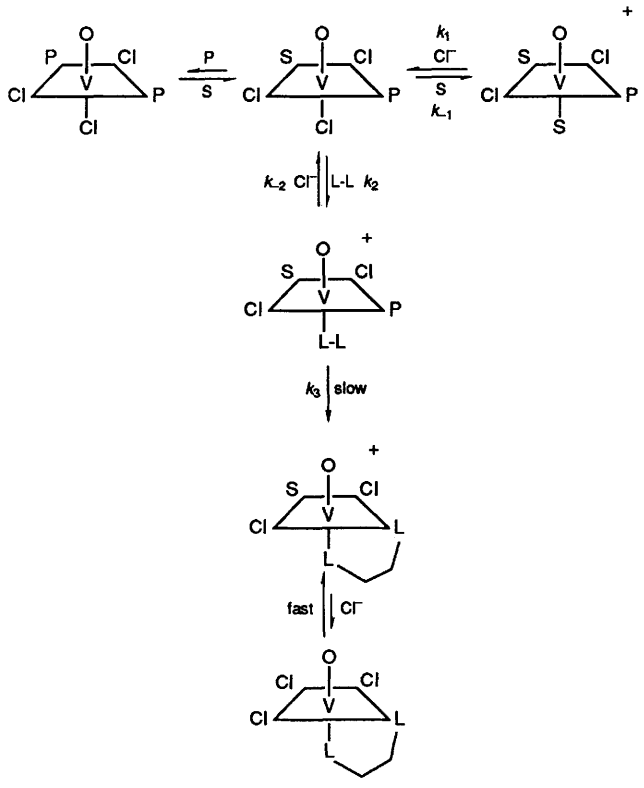
Fig. 2 Dependence of $1/k_{obs}$ on $1/[Cl^-]$ for the reaction of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with 2,2′-bipyridine at 25 °C in thf. The data shown are $[Cl^-]$ = 1.0–10.0, [bipy] = 5.0 (■), 10.0 (●) or 40.0 mmol dm^{-3} (▲); lines drawn are those defined by equation (3). The inset shows the corresponding dependence of $[bipy]/k_{obs}$ on $1/[Cl^-]$

from the dependence on the concentration of bipy. However, as can be seen from Fig. 2 (insert), when the concentration of bipy is constant, a graph of $[bipy]/k_{obs}$ against $1/[Cl^-]$ gives a straight line (for each [bipy]). Each line has a common intercept and a gradient which shows only a slight dependence on the concentration of bipy. This slight variation in the gradient can be fitted to the expression $\{1 + (18.8 \pm 0.2)[bipy]\}/(5.8 \pm 0.2) \times 10^4$, and hence the derived, generalised, rate equation in the presence of chloride is as in (3). This expression has been

$$k_{obs} = \frac{(5.8 \pm 0.2) \times 10^4[bipy][Cl^-]}{1 + (18.8 \pm 0.2)[bipy] + (7.4 \pm 0.2) \times 10^2[Cl^-]} \quad (3)$$

used to predict the lines for the reaction kinetics when the concentration of chloride is kept constant, and the concentration of bipy varied, as shown in Fig. 1.

Kinetics with depe.—The reaction between *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ (5.0×10^{-4} mol dm^{-3}) and depe (5–50 mmol dm^{-3}) exhibits a single-exponential absorbance–time curve, with an initial absorbance which is that of the parent complex and a final absorbance which is that of $[VCl_3(OPMe_2Ph)(depe)]$ in thf. The kinetics of the reaction is independent of the concentration of depe in the range studied, and shows a first-order dependence on the concentration of complex. These data are collected in Table 2. This simple kinetics is perturbed by the addition of $[PBu_4]Cl$ and, as



Scheme 1 Mechanism for the reaction of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ with L–L = bipy or depe in thf. Only the donor atoms of the ligands are shown, for clarity

shown by the data in Table 2, exhibits a first-order dependence on chloride-ion concentration, with the corresponding rate equation (4).

$$k_{obs} = (2.6 \pm 0.4) \times 10^3[Cl^-] \quad (4)$$

Discussion

The overall reaction that is being studied in these reactions is the displacement of the monotertiary phosphine ligands by a bidentate ligand at an octahedral, fourteen-electron, vanadium(III) site, and as such is adequately described by equation (1). However, it has been shown[1] that the solid-state structure established for the parent complex is not retained in thf solution, and that the predominant solution species is $[VCl_2(OPMe_2Ph)(PMe_2Ph)(thf)_2]^+$. The following discussion will assume that this solvento-cation is the reactive species in the substitution reactions, a proposal which is borne out by the succeeding kinetic analysis. The nature of $[VCl_3(OPMe_2Ph)(L–L)]$ (L–L = bipy or depe) in solution will be discussed below, since the kinetics also indicates an important feature concerning these species.

It is most convenient to start discussing the kinetics for the various reactions by looking at the studies with bipy, since it is with this substrate that the most complicated rate law is observed.

The generalised rate equation (3) reveals that chloride both accelerates and inhibits the reaction, and thus a mechanism involving chloride in the two roles is defined. Furthermore since the numerator contains both chloride and bipy concentrations, both must be bound to vanadium prior to the rate-limiting step.[7] In addition since the denominator of equation (3) contains terms dependent on the concentration of chloride or bipy (but not on both) this rate equation is consistent with the mechanism shown in Scheme 1.

In this mechanism there is a single pathway by which the substitution is accomplished, all steps of which are associative. In the initial stage, $[VCl_2(OPMe_2Ph)(PMe_2Ph)(thf)_2]^+$ reacts with chloride ion to displace a molecule of solvent and generate $[VCl_3(OPMe_2Ph)(PMe_2Ph)(thf)]$ and it is this species which now reacts with bipy by displacing chloride to form $[VCl_2(OPMe_2Ph)(PMe_2Ph)(thf)(bipy)]^+$ in which the bipy ligand is only monodentate. Subsequent rate-limiting ring closure of bipy displacing PMe_2Ph and rapid attack by chloride ion completes the reaction.

Application of the steady-state treatment to the mechanism in Scheme 1 yields the rate equation (5), of identical form to (3).

$$k_{obs} = \frac{k_1k_2k_3[L–L][Cl^-]}{k_{-1}k_3[thf] + k_2k_3[L–L] + k_{-1}k_{-2}[Cl^-][thf]} \quad (5)$$

Comparison of equations (3) and (5) allows the determination of the values for L–L = bipy, $k_1k_2/k_{-1}[thf] = (5.8 \pm 0.2) \times 10^4$ dm^6 mol^{-2} s^{-1}, $k_2/k_{-1}[thf] = 18.8 \pm 0.2$ dm^3 mol^{-1}, $k_2/k_3 = (7.4 \pm 0.2) \times 10^2$ dm^3 mol^{-1} and $k_1 = (3.1 \pm 0.2) \times 10^3$ dm^3 mol^{-1} s^{-1} (where the concentration of thf in thf is 15.7 mol dm^{-3}). The limited data on the substitution patterns at vanadium(III) centres prohibit a detailed discussion on these elementary rate constants; this problem is further compounded by the unknown labilities and electronic influences of the various coligands.

There are several limiting forms of equation (5), but only two of these are relevant to the discussion of the rate laws observed in these substitution reactions. The first arises when the chloride-ion concentration is low, that is in the studies without $[PBu_4]Cl$ being present. In this case the chloride ion-dependent term in the denominator is small compared with the other terms and hence equation (6) is valid. At a constant

$$k_{obs} = \frac{k_1k_2[L–L][Cl^-]}{k_{-1}[thf] + k_2[L–L]} \quad (6)$$

concentration of complex the chloride-ion concentration is constant ([V] = [Cl$^-$], for one chloride ion liberated upon dissolution of the parent complex in thf). Thus equation (6) is of the same form as (2); furthermore since [V] = [Cl$^-$] = 2.5×10^{-4} mol dm^{-3} the values $k_1k_2[Cl^-]/k_{-1}[thf] = 14.5 \pm 0.2$ dm^3 mol^{-1} s^{-1} and $k_2/k_{-1}[thf] = 18.8 \pm 0.2$ dm^3 mol^{-1} can be calculated for L–L = bipy in good agreement with the values shown in equation (2). However, it is quite clear that since the absorbance *vs.* time traces observed under these conditions are single exponentials, chloride cannot be consumed in the overall reaction. This also is consistent with the mechanism shown in Scheme 1. Although thf is not a good solvent to establish conductivities, the conductivity of $[VCl_3(OPMe_2Ph)(bipy)]$ in thf ($\Lambda_M = 30$ ohm^{-1} cm^2 mol^{-1}) indicates appreciable ionic character in solution.

The second limiting form of equation (5) arises when the value of the denominator is dominated by the L–L dependent term. This can occur when the concentration of L–L is very high, or when the nucleophilicity of L–L is high. Under these conditions the reaction is rate-limited by the initial displacement of co-ordinated thf by chloride ion in $[VCl_2(OPMe_2Ph)(PMe_2Ph)(thf)_2]^+$ and equation (5) reduces to (7). This is of the

$$k_{obs} = k_1[Cl^-] \quad (7)$$

same form as that observed in the studies with depe and shown in equation (4). Furthermore the value $k_1 = (3.1 \pm 0.2) \times 10^3$ dm^3 mol^{-1} s^{-1}, derived from the generalised equation (5), is in good agreement with the value in (4). Thus all the rate laws observed in the substitution reactions of this vanadium(III) centre can be accounted for by a single mechanism and the generalised rate equation (5).

One of the most interesting aspects of this work is the observation that $[VCl_2(OPMe_2Ph)(PMe_2Ph)(thf)_2]^+$ does not

react directly with bipy or depe, but rather must undergo a prior reaction with chloride ion. Presumably the bulk of the two thf ligands inhibits direct attack by bipy or depe, and replacement of one of the thf ligands by the less sterically demanding chloro-group renders the site more susceptible to nucleophilic attack. *Nevertheless*, the chloro-group is not bound very tightly since it is chloride which is displaced by the nucleophile, and in the true sense that is chloride-catalysed nucleophilic attack. Incidentally, the observation that the binding of chloride ion to the vanadium centre occurs prior to the reaction with nucleophile further substantiates the conclusion[1] that the dominant solution species is a solvento-cation. Finally, that the solvento-cationic species is not an intermediate in the substitution reactions is less consistent with a dissociative mechanism, and more indicative of an associative pathway for the reasons based on steric congestion outlined above.

In more general terms the associative steps in this multistep substitution reaction, and the exchange and substitution reactions of $[V(OH_2)_6]^{3+}$, reflect the reactivity of the various possible transition states leading from the fourteen-electron species to products. Clearly a reaction profile *via* a seven-co-ordinate, sixteen-electron species is energetically more favourable than a reaction *via* a five-co-ordinate, twelve-electron species.

Finally there is a stereochemical aspect of Scheme 1 which needs to be clarified. Although rate equation (5) defines a mechanism in which bipy displaces chloride ion, it is not unambiguous which chloro-group it is. In Scheme 1 is shown the position of displacement which we most favour: the chloro-group *trans* to the phosphine oxide. This position is favoured since subsequent ring closure of bipy or depe must result in the *mer* isomer, the structure established by X-ray crystallography for $[VCl_3(OPMe_2Ph)(depe)]$.[1] Initial displacement of either chloro-groups *cis* to the phosphine oxide could result in the *fac* isomer. The observation that in solution *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$ (with a chloro-group *trans* to the phosphine oxide) is a 1:1 electrolyte whereas *mer*-$[VCl_3(OPMe_2Ph)(depe)]$ (with all chloro-groups *cis* to the phosphine oxide) is a non-electrolyte is consistent with a labilising influence by a *trans*-phosphine oxide. However, if the chloro-group *trans* to the phosphine oxide is the one most readily displaced, no ground-state bond weakening is reflected in the crystal structure of *trans,mer*-$[VCl_3(OPMe_2Ph)(PMe_2Ph)_2]$,[1] but of course this is not an essential pre-requisite for an associative mechanism. We must treat this stereochemical implication of these substitution reactions with some caution based, as it is, on solid-state structural determinations.

Experimental

All manipulations of solutions and compounds were performed under an atmosphere of dinitrogen, using standard Schlenk-tube and syringe techniques.

The preparation and characterisation of all vanadium complexes used in this paper have already been described.[1] The compounds, $[PBu_4]Cl$ and [bipy] (both from Aldrich) were used as received; depe[8] and PMe_2Ph[9] were prepared in this laboratory.

Kinetic Studies.—All kinetic studies were performed in thf, freshly distilled from sodium–benzophenone. All reactions were studied under pseudo-first-order conditions, and the stopped-flow traces collected and analysed on a BBC microcomputer. All traces were good exponentials for at least three half-lives. The kinetics was studied on an Aminco-Morrow stopped-flow apparatus modified to study air-sensitive materials as described earlier.[10]

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