A Nuclear Magnetic Resonance Study of Trimethyl Phosphate Exchange on the Hexakis(trimethyl phosphate)scandium(III) Ion

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^{1}H N.m.r. lineshape analysis methods have been used to investigate the exchange of tmp (trimethyl phosphate) on $[Sc(tmp)_6]^{3+}$ in CD_3CN, sym-$C_2H_2Cl_4$, and CD_3NO_2 solvents. In the first two solvents the rate of tmp exchange on $[Sc(tmp)_6]^{3+}$ is virtually independent of [tmp] and, typically, k_{ex} (300 K) = exchange rate/6$[Sc(tmp)_6{}^{3+}]$ = 65.7 ± 2.6 s^{-1}, $\Delta H^‡$ = 29.8 ± 0.4 kJ mol^{-1}, and $\Delta S^‡$ = −111 ± 2 J K^{-1} mol^{-1} when $[Sc(tmp)_6{}^{3+}]$, [tmp], and $[CD_3CN]$ are 0.110 0, 0.693, and 15.0 mol dm^{-3} respectively. In CD_3NO_2 solvent the exchange rate = $6k'_{ex}[Sc(tmp)_6{}^{3+}][tmp]$ and k'_{ex} (300 K) = 51.3 ± 1.8 dm^3 mol^{-1} s^{-1}, $\Delta H^‡$ = 26.0 ± 0.9 kJ mol^{-1}, and $\Delta S^‡$ = −126 ± 3 J K^{-1} mol^{-1}. The mechanistic implications of these rate laws are discussed.

THE rate of murexide substitution[1] into the first co-ordination sphere of the aquascandium(III) ion [k(285 K) = 4.8×10^7 dm^3 mol^{-1} s^{-1}] is unexpectedly fast for a trivalent metal ion occurring early in the Periodic Table. It has been suggested that this may be a consequence of there being more than six aqua-ligands in the first co-ordination sphere of scandium(III) in solution,[2] but only 5.1 aqua-ligands have been directly detected in that environment, possibly as a result of some of the first co-ordination sphere sites being occupied by anionic ligands.[3] In the solid state, six, eight, and nine oxygen donor atoms occupy the first co-ordination sphere of acetylacetonato-,[4] tropolonato-,[5] and nitrato-complexes[6] of scandium(III). Thus there exists considerable uncertainty concerning the nature of ligand substitution processes involving scandium(III) species. Accordingly we now report a detailed study of ligand exchange on the hexakis(trimethyl phosphate)scandium(III) ion, $[Sc(tmp)_6]^{3+}$.

EXPERIMENTAL

The complex $[Sc(tmp)_6][ClO_4]_3$ was prepared by refluxing hydrated scandium(III) perchlorate (G. Frederick Smith) (2.5 g) with triethyl orthoformate[7,8] (15 g) at 330 K for 1 h after which distilled and dried (Linde 4A molecular sieves) tmp (4.6 g) was added at room temperature under a dry nitrogen atmosphere. The white crystalline product was filtered off, washed with anhydrous ether, and subsequently vacuum-dried {Found: C, 18.35; H, 4.60; P, 15.4; Sc, 3.80. $[Sc(tmp)_6][ClO_4]_3$ requires C, 18.25; H, 4.60; P, 15.7; Sc, 3.80%}. Analyses for Sc^{3+} were performed using an ion-exchange technique[9] and the C, H, and P analyses were carried out by the Australian Microanalytical Service, Melbourne. All preparative and handling procedures except those mentioned as being performed under vacuum were carried out under dry nitrogen.

Solutions of $[Sc(tmp)_6][ClO_4]_3$ and tmp in distilled and dried CD_3CN, CD_3NO_2, or sym-$C_2H_2Cl_4$ were prepared in 2- or 5-cm^3 volumetric flasks immediately prior to the n.m.r. experiments. Portions of each solution were degassed and sealed under vacuum in 5-mm o.d. n.m.r. tubes.

^{1}H (90 MHz) and ^{31}P (36.4 MHz with ^{1}H broad-band decoupling) n.m.r. spectra were run on a Brüker HX90E spectrometer in PFP and PFT modes respectively, using the ^{2}H resonances of CD_3CN and CD_3NO_2, and the ^{1}H resonance of $C_2H_2Cl_4$, as locking signals. Computer-averaged PFP and PFT spectra for each temperature were stored on a magnetic disk. The ^{1}H spectra were later subjected to complete lineshape analysis using the BNC-12 minicomputer of the spectrometer. The spectrometer temperature control was better than ±0.3 K and the variable temperature probe was calibrated with a copper–constantan thermocouple.

Solution composition and kinetic parameters for tmp exchange on $[Sc(tmp)_6]^{3+}$

Solution	$[Sc(tmp)_6{}^{3+}]$	$[tmp]_{free}$	$[CD_3CN]$	$[C_2H_4Cl_2]$	$[CD_3NO_2]$	k_{ex} (300 K) [a]	$\Delta H^‡$ [b]	$\Delta S^‡$ [b]	
No.			mol dm^{-3}			s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	c.n. [c]
(1)	0.110 0	0.693	15.0			65.7 ± 2.6	29.8 ± 0.4	−111 ± 2	5.9 ± 0.1
(2)	0.050 3	0.147	17.3			36.5 ± 0.7	31.3 ± 0.2	−111 ± 1	5.8 ± 0.2
(3)	0.017 4	0.109	17.7			33.9 ± 1.2	32.7 ± 0.3	−107 ± 1	6.0 ± 0.2
(4)	0.015 3	0.044 8	17.7			33.4 ± 1.1	33.2 ± 0.4	−105 ± 2	5.8 ± 0.2
(5)	0.003 07	0.019 3	18.1			36.3 ± 1.2	28.9 ± 0.3	−119 ± 1	6.1 ± 0.1
(6)	0.001 09	0.006 9	18.1			49.2 ± 2.3	29.4 ± 0.6	−115 ± 2	6.0 ± 0.2
(7)	0.113	0.864		7.32		42.4 ± 1.3	41.3 ± 0.5	−76.0 ± 1.8	6.0 ± 0.1
(8)	0.057 9	0.386		8.11		42.7 ± 1.6	43.4 ± 0.5	−69.1 ± 1.8	6.1 ± 0.2
(9)	0.125	0.892			14.0				5.9 ± 0.1
(10)	0.107	0.595			14.9	k'_{ex} (300 K) [d] = 51.3 ± 1.8 dm^3 mol^{-1} s^{-1}			5.9 ± 0.1
(11)	0.061 2	0.312			16.1	$\Delta H^‡$ [d] = 26.0 ± 0.9 kJ mol^{-1}			6.0 ± 0.1
(12)	0.027 9	0.199			16.9	$\Delta S^‡$ [d] = −126 ± 3 J K^{-1} mol^{-1}			6.1 ± 0.2
(13)	0.004 4	0.031 5			17.7				6.0 ± 0.2

[a] k_{ex} (300 K) interpolated from the Eyring plots. The quoted errors represent one standard deviation. [b] $\Delta H^‡$ and $\Delta S^‡$ determined from the Eyring plots. The quoted errors represent one standard deviation. [c] c.n. = number of co-ordinated tmp molecules as determined from n.m.r. integration in the slow-exchange temperature region. [d] The quoted errors are based on an assumed maximum error of 10% in any observed τ_C value.

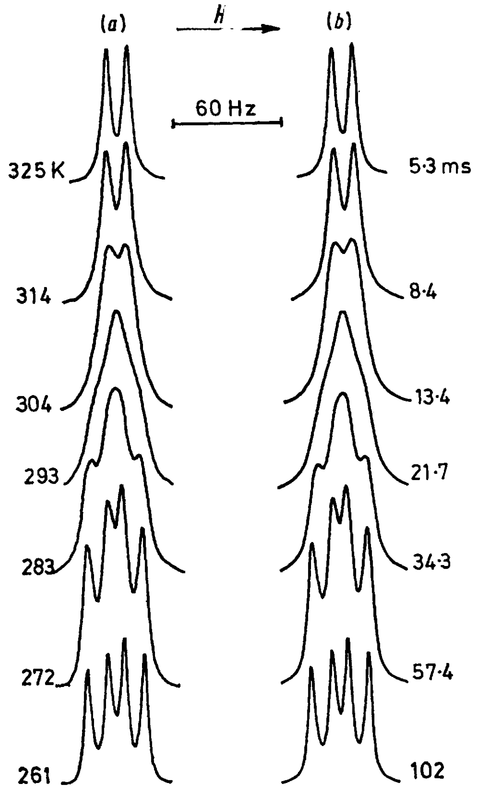

FIGURE 1 Experimental (*a*) and computed (*b*) best-fit ^1H n.m.r. lineshapes for solution (1). The experimental temperatures and best-fit τ_C values appear to the left and right of the Figure, respectively. The co-ordinated tmp signal is downfield

RESULTS AND DISCUSSION

Solutions of $[Sc(tmp)_6][ClO_4]_3$ and tmp in CD_3CN, CD_3NO_2, and $C_2H_2Cl_4$ solvents exhibited a ^1H n.m.r. doublet for co-ordinated tmp downfield from the doublet of free tmp under conditions of slow exchange between the co-ordinated and free sites. The slow exchange condition was observed in all the CD_3CN and $C_2H_2Cl_4$ solutions (Table) below 250 and 260 K respectively. In CD_3NO_2 solutions the onset of the slow exchange condition occurred at progressively higher temperatures as [tmp] decreased; thus slow exchange was observed at and below 265 and 305 K respectively for the concentration extremes represented by solutions (9) and (13). In every case only one co-ordinated tmp doublet was observed and a comparison of the integrated areas of the co-ordinated and free doublets indicated that, within experimental error, six tmp ligands occupy the first co-ordination sphere of scandium(III), as indicated in the Table. Coalescence of the co-ordinated and free tmp doublets occurred as the temperature was raised as exemplified by the $[Sc(tmp)_6]^{3+}$–tmp–CD_3CN system in Figure 1. This phenomenon was consistent with tmp exchange occurring between the co-ordinated and free sites, and the best-fit mean lifetime of a single tmp ligand in $[Sc(tmp)_6]^{3+}$, τ_C was determined at each temperature by a complete lineshape analysis of the experimental spectrum using a computer program based upon the exchange-modified Bloch equations.[10] Input parameters for this program included the chemical shifts between the doublets, the linewidths at half amplitude pertaining to each signal in the absence of site exchange for each experimental temperature, and the site populations. For the example shown in Figure 1, the chemical shift between the free and bound doublets varied from 20.0 Hz at 230 K to 20.3 Hz at 246 K. The chemical shifts and linewidths were extrapolated (against $1/T$) from the slow-exchange region.

The co-ordinated and free-site lifetimes, τ_C and τ_F respectively, are related through equation (1) where x_C

$$\tau_C/x_C = \tau_F/x_F = 1/k_{ex}x_C \qquad (1)$$

and x_F are the mol fractions of co-ordinated and free tmp, and the observed first-order rate constant, k_{ex}, is given by equation (2). A plot of $\tau_C T$ against $1/T$ for

$$k_{ex} = (k_b T/\mathbf{h})\exp(-\Delta H^\ddagger/RT)\exp(\Delta S^\ddagger/R) \qquad (2)$$
$$= \text{exchange rate}/6[Sc(tmp)_6{}^{3+}]$$

the CD_3CN and $C_2H_2Cl_4$ solutions is shown in Figure 2 and the derived kinetic parameters are given in the Table.

From the data it is seen that k_{ex} (300 K) in CD_3CN solutions varies by a factor of two in a non-linear manner over a hundred-fold variation in [tmp], which indicates that the rate of the predominant exchange process is independent of [tmp]. This observation is typical of a dissociative (*D*) exchange mechanism[11] in which the rate-determining step is the breaking of a metal–ligand bond to produce a reactive intermediate $[Sc(tmp)_5]^{3+}$.

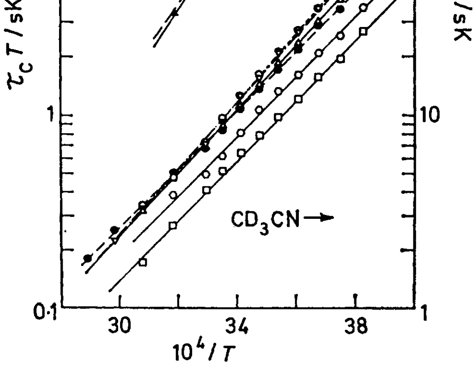

FIGURE 2 Semi-logarithmic plots of $\tau_C T$ against $1/T$ for the $[Sc(tmp)_6]^{3+}$–tmp–CD_3CN and $[Sc(tmp)_6]^{3+}$–tmp–$C_2H_2Cl_4$ systems. Data for solutions (1)—(8) are represented as (1) —□—, (2) —△—, (3) —·—▽—·—, (4) - - -○- - -, (5) ——●——, (6) —⬡—, (7) ——▼——, and (8) —▲—

Such a mechanism is characterised by a rate law of the same form as equation (2) except that $k_{ex} = k$, the first-order rate constant for the unimolecular rate-determining step. {As will be noted later, the dynamics of tmp exchange on $[Sc(tmp)_6]^{3+}$ appear to be dictated by the nature of the solvent and it is therefore likely that a part of the observed variation in k_{ex} (300 K) for solutions (1)—(6) reflects composition changes in bulk solvent as both [tmp] and $[Sc(tmp)_6{}^{3+}]$ are varied.}

Alternatively, the dissociative interchange[11] (I_d) mechanism, as shown in equation (3), can give rise to the observed exchange rate law. In this formalism, metal–ligand bond breaking remains the predominant contribution to the activation energetics but tmp exchange occurs within an encounter complex $[Sc(tmp)_6]^{3+} \cdots tmp$ consisting of $[Sc(tmp)_6]^{3+}$ with a tmp molecule residing in the second co-ordination sphere. The I_d mechanistic scheme is represented in equation (3)

$$[ScL_6]^{3+} + L^* \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [ScL_6]^{3+} \cdots L^* \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} [ScL_5L^*]^{3+} + L \quad (3)$$

where L = tmp, $K = [ScL_6{}^{3+} \cdots L]([ScL_6{}^{3+}][L])^{-1}$, k is the specific rate constant for ligand interchange between the first and second co-ordination spheres of the encounter complex, and the asterisk is a typographical distinction only. The observed first order exchange rate constant, k_{ex}, arising from the I_d mechanism is given by equation (4). When (*a*) $K[L] \gg 1$,

$$k_{ex} = kK[L](1 + K[L])^{-1} \quad (4)$$

$k_{ex} = k$ and the tmp exchange rate becomes independent of [tmp] as observed in CD_3CN solution; and when (*b*) $K[L] \ll 1$, $k_{ex} = kK[L]$. An inspection of the relative tmp and CD_3CN concentrations in the Table indicates that a high degree of preferential occupancy of the second co-ordination sphere of scandium(III) by tmp would be necessary for limiting condition (*a*) to hold over the entire experimental concentration range. There is no experimental evidence that such preferential occupancy occurs in this system.

Two solutions in $C_2H_2Cl_4$ were studied, and the derived $\Delta H^‡$ and $\Delta S^‡$ values are seen to be markedly different from those in CD_3CN for tmp exchange on $[Sc(tmp)_6]^{3+}$. Unfortunately, the lineshape coalescence phenomena became irreproducible in less concentrated solutions after they had been taken above 320 K, thus precluding exchange studies over a greater concentration range. It is possible that some decomposition of $C_2H_2Cl_4$ occurred, leading to the generation of chloride ion which subsequently co-ordinated to scandium(III). The coalescence phenomena for the two solutions (7) and (8) in the Table, however, were reproducible after several days at room temperature. The k_{ex} values of these solutions appear to be independent of [tmp], but the two-fold concentration range is too small to base a definite mechanistic conclusion on.

In CD_3NO_2 solution, the dynamics of the tmp exchange process (Figure 3) were characterised by a second-order rate law [equation (5)] over the 28.3-fold variation in [tmp] examined (Figure 3), and the derived kinetic parameters are given in the Table. Equation (5) is consistent with either an I_d mechanism [equation (4)] in

$$\text{Exchange rate} = 6k'_{ex}[Sc(tmp)_6{}^{3+}][tmp] \quad (5)$$

the limit (*b*) or an associative (*A*)[11] mechanism in which the rate-determining step is the formation of a transition state or reactive intermediate of stoicheiometry $[Sc(tmp)_7]^{3+}$. In view of their similar molecular sizes and dielectric constants (35.9 and 36.2 for their respective proton analogues at 298 K) it is surprising that different tmp exchange rate laws should be observed in the solvents CD_3CN and CD_3NO_2. The least mechanistic difference arises if the I_d mechanism in the limits (*a*) and (*b*) operates in CD_3CN and CD_3NO_2 respectively, whereas the greatest mechanistic difference arises if *D* and *A* mechanisms operate in these solvents respectively. However, it is not possible to test for the *A* mechanism in this system by observing the effect of variation in the character of an incoming ligand upon the substitution rate.

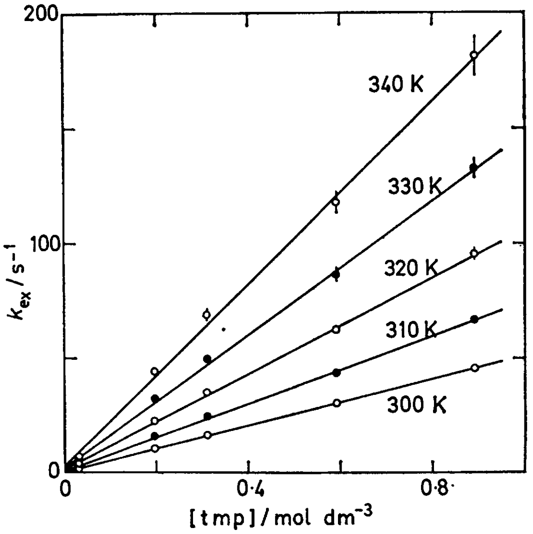

FIGURE 3 Plots of k_{ex} data sets against [tmp] for the $[Sc(tmp)_6]^{3+}$–tmp–CD_3NO_2 system. The solid lines represent linear regression lines for the expression $k_{ex} = k'_{ex}[tmp]$. k_{ex} (= $1/\tau_C$) was interpolated at each temperature from the linear regression line of ln $\tau_C T$ against $1/T$ for each of the solutions (9)—(13)

Clearly the nature of the solvent has a significant effect upon the kinetics of the tmp exchange process, but low-temperature ^1H n.m.r. spectra of $[Sc(tmp)_6][ClO_4]_3$ in mixtures of CD_3CN and CH_3CN, or CD_3NO_2 and CH_3NO_2, exhibited no resonances attributable to either solvent being present in the first co-ordination sphere of scandium(III). This observation, in conjunction with the observed constancy of the co-ordination number of scandium(III) (Table) with respect to tmp over extended concentration ranges, indicates that the entry of solvent into the first co-ordination sphere is probably not a significant consideration. Nevertheless the solvent does have a marked effect upon the chemical shift of [Sc(tmp)$_6$]$^{3+}$ with respect to that of free tmp. Thus, in CD_3CN, $C_2H_2Cl_4$, and CD_3NO_2, the ^1H chemical shift of [Sc(tmp)$_6$]$^{3+}$, which is slightly temperature dependent as mentioned earlier, ranges from 0.224—0.199 p.p.m. for solutions (1)—(6) (240 K); 0.221—0.216 p.p.m. for solutions (7)—(8) (240 K); and 0.329—0.337 p.p.m. for solutions (9)—(13) (260 K), downfield from the free tmp resonance. In CD_3CN and $C_2D_2Cl_4$ the ^{31}P chemical shift of [Sc(tmp)$_6$]$^{3+}$ is 7.46 and 7.60 p.p.m. upfield from the free tmp resonance at 235 K whereas in CD_3NO_2 it is 1.98 p.p.m. downfield at 260 K. The CD_3NO_2 solutions freeze below 250 K but as the ^{31}P chemical shift has only a small temperature variation the chemical shift of [Sc(tmp)$_6$]$^{3+}$ extrapolated to 235 K would be close to 1.98 p.p.m. downfield from free tmp. {The [Sc(tmp)$_6$]$^{3+}$ ^{31}P resonance is a broad octuplet, when proton-decoupled, for which $J(^{45}Sc-^{31}P)$ is *ca.* 35 Hz.[12]} The different chemical shifts observed may be indicative of marked differences in the solvent interactions with co-ordinated and free tmp in CD_3CN and CD_3NO_2, and it is particularly interesting that the chemical shifts in the latter solvent, in which second-order exchange kinetics dominate, are distinctly different from those observed in the other two solvents. Whether or not the effect of solvent upon the free energies of ground and transition states is sufficient to cause a change from a *D* to an *A* mechanism for tmp exchange cannot be determined unequivocally from the present data. The observation of ground state co-ordination numbers of six,[4] eight,[5] and nine [6] for scandium(III) in the solid state suggests that the possibility of such a mechanistic change exists, however.

The $\Delta G^\ddagger$ (300 K) for tmp exchange on [Sc(tmp)$_6$]$^{3+}$ in CD_3CN, averaged over solutions (1)—(6), is 64.2 kJ mol^{-1} and the analogous value for the $C_2H_2Cl_4$ solutions is 64.1 kJ mol^{-1}. These values are intermediate in magnitude between those for [Mg(tmp)$_6$]$^{2+}$ in CD_2Cl_2 solution,[13] $\Delta G^\ddagger$ (300 K) = 39.5 kJ mol^{-1}, and [Al(tmp)$_6$]$^{3+}$ in either CH_3NO_2 [14] or CD_3NO_2 [15] solution for which $\Delta G^\ddagger$ (300 K) = 75.6 and 76.6 kJ mol^{-1}, respectively. Both these species are considered to undergo ligand exchange through a dissociative process for which the surface charge density of the metal centre is thought to be a major determinant of $\Delta G^\ddagger$.[16-18] On this basis the $\Delta G^\ddagger$ values observed for [Sc(tmp)$_6$]$^{3+}$ fall qualitatively in the range expected for a six-co-ordinate tervalent metal ion of radius 0.68 Å (Mg^{2+} and Al^{3+} radii are 0.78 and 0.45 Å, respectively). It is pertinent to note, however, the mechanistic differences between ligand exchange on [Al(tmp)$_6$]$^{3+}$ and [Sc(tmp)$_6$]$^{3+}$ in CH_3NO_2 and CD_3NO_2 solutions, respectively. In the former system the exchange rate is independent of [tmp] whereas in the latter system it is linearly dependent upon [tmp]. The two complexes are of similar size and it is therefore improbable that tmp will preferentially enter the second co-ordination sphere of the aluminium(III) species, thus indicating that the least difference in mechanism between the two systems is between the *D* mechanism for [Al(tmp)$_6$]$^{3+}$ and the I_d mechanism for [Sc(tmp)$_6$]$^{3+}$. The larger ionic radius of scandium(III) will presumably cause [Sc(tmp)$_5$]$^{3+}$ and [Sc(tmp)$_7$]$^{3+}$ to be respectively less and more stable than their aluminium(III) analogues, with a consequently greater tendency for [Sc(tmp)$_6$]$^{3+}$ to undergo ligand exchange through either an I_d or an *A* mechanism.

It is clear that [Sc(tmp)$_6$]$^{3+}$ is not unexpectedly labile by comparison with its aluminium(III) and magnesium(II) analogues, and whilst the relatively greater lability of the aquascandium(III) species may well be attributable to that species having a co-ordination number greater than six,[1,2] the possibility of an associative ligand substitution process characterised by a large second-order rate constant occurring on [Sc(OH$_2$)$_6$]$^{3+}$ should not be overlooked.

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