Proton Magnetic Resonance Study of the Exchange of Trimethyl Phosphate on the Tetrakis(trimethyl phosphato)beryllium(II) Complex

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The exchange of trimethyl phosphate in the complex $[Be\{(MeO)_3PO\}_4]^{2+}$ is characterised by the rate law (i),

$$\text{Rate} = 4k_{ex}[Be\{(MeO)_3PO\}_4{}^{2+}] \qquad \text{(i)}$$

where k_{ex} (298 K) = 3·6 ± 0·6 s^{-1}, $\Delta H^‡$ = 56·9 ± 4·2 kJ mol^{-1}, and $\Delta S^‡$ = −43·9 ± 12·6 J K^{-1} mol^{-1} are typical values observed in the presence of methylene chloride diluent. The observed zero-order exchange-rate dependence on the concentration of free trimethyl phosphate is considered symptomatic of a dissociative trimethyl phosphate exchange mechanism.

AN understanding of the mechanism of solvent exchange, apart from its own intrinsic interest, appears to be fundamental to the interpretation of ligand-substitution processes on metal ions in solution.[1-3] Many kinetic studies of solvent exchange have been reported,[4,5] but in very few cases has the kinetic order with respect to the solvent been determined.[6] A study of the exchange of trimethylphosphate in the complex $[Be\{(MeO)_3PO\}_4]^{2+}$ in the presence of methylene chloride diluent, in which the kinetic order with respect to trimethyl phosphate is shown to be zero, is reported here.

RESULTS AND DISCUSSION

Under slow exchange conditions the doublet of co-ordinated trimethyl phosphate in the complex $[Be\{(MeO)_3PO\}_4]^{2+}$ appeared downfield from the doublet arising from bulk trimethyl phosphate in the ^1H n.m.r. spectrum as seen in Figure 1. Over a 50 K temperature range, below the temperature at which chemical-exchange-induced spectral modification occurred (*ca.* 303 K), a comparison of the integrated areas of the two doublets gave a co-ordination number [7] of four for beryllium(II) in all solutions studied. Typical values are given in the Table. No signal attributable to co-ordinated methylene chloride was observed, and it was concluded that $[Be\{(MeO)_3PO\}_4]^{2+}$ is the only significant complex in the solutions investigated. Beryllium(II) is also reported to co-ordinate four solvent molecules in water,[8] dimethylformamide,[9] and in water–hexamethylphosphoramide [10] mixtures. By contrast magnesium(II),[11] aluminium(III), gallium(III), and indium(III) [12] co-ordinate six trimethyl phosphate molecules in solution.

Kinetic parameters for trimethyl phosphate exchange were derived from the coalescing trimethyl phosphate doublets using a complete signal-shape analysis. A computer program, based upon that of Siddall *et al.*,[13] was used to generate signal shapes corresponding to given trimethyl phosphate exchange rates. A subroutine employed, which selected calculated signal shapes giving the best fit to experimental signal shapes, was a modification to the original program. Typical experimental and best-fit calculated line shapes generated by a CDC 6400 computer are shown in Figure 1. The mean life-times of trimethyl phosphate in the complex $[Be\{(MeO)_3PO\}_4]^{2+}$, τ_C, and of bulk trimethyl phosphate, τ_B, are related by equation (1), where x_C and x_B are the

$$\tau_C/x_C = \tau_B/x_B = 1/k_{ex}x_C \qquad (1)$$

appropriate mole fractions and k_{ex} is a first-order exchange rate constant which may be expressed as in equation (2).

$$k_{ex} = (\boldsymbol{k}T/\boldsymbol{h})\exp(-\Delta H^‡/RT)\exp(\Delta S^‡/R) \qquad (2)$$

The composition of the $[Be\{(MeO)_3PO\}_4]^{2+}$ solutions are given in the Table. The k_{ex} values determined at various temperatures from solutions (i)—(iv), all of which contain methylene chloride diluent, fall close to a single curve. In Figure 2 these data are plotted, and the solid lines represent the least-squares fit to each data set. The derived kinetic parameters listed in the Table are seen to be almost identical within experimental error. The virtual independence of concentration and reactant mole ratio of the kinetic parameters

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[1] D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45.

[2] K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**. 107.

[3] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2198. H. P. B. and E. F. C. base their discussion on $\Delta S^‡$ values calculated from second-order rate constants, whereas in ref. 11 and in this work $\Delta S^‡$ values are calculated from first-order rate constants. The general postulates of the H.P.B.–E.F.C. model are unaffected by the difference.

[4] T. R. Stengle and C. H. Langford, *Co-ordination Chem. Rev.*, 1967, **2**, 349.

[5] J. P. Hunt, *Co-ordination Chem. Rev.*, 1972, **7**, 1.

[6] L. S. Frankel, *Chem. Comm.*, 1969, 1254. In this reference the residence time of dimethyl sulphoxide (dmso) on the complex in $[Ni(dmso)_6]^{2+}$ is shown to be independent of [dmso] over the range 0·6—2·2M in nitromethane and methylene chloride inert diluents. The ^1H n.m.r. kinetic method (T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **41**, 2553) employed requires that not more than 10% of the total [dmso] be co-ordinated. Langford and Tsiang (*Inorg. Chem.*, 1969, **9**, 2346) subsequently demonstrated that no significant preferential solvation of $[Ni(dmso)_6]^{2+}$ by dmso occurred under these experimental conditions, and concurred with Frankel's interpretation of the dmso exchange data in terms of a dissociative mechanism.

[7] S. F. Lincoln, *Co-ordination Chem. Rev.*, 1971, **6**, 309.

[8] R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, 1963, **39**, 1349.

[9] N. A. Matwiyoff and W. G. Movius, *J. Amer. Chem. Soc.*, 1967, **89**, 6077.

[10] C. Beguin, J. J. Delpuech, and A. Peguy, *Mol. Phys.*, 1969, **17**, 317.

[11] J. Crea, S. F. Lincoln, and R. J. West, *Austral. J. Chem.*, 1973, **26**, 1227.

[12] J. Crea and S. F. Lincoln, *Inorg. Chem.*, 1972, **11**, 1131.

[13] T. H. Siddall, W. E. Stewart, and F. D. Knight, *J. Phys. Chem.*, 1970, **74**, 3580.

for solutions (i)—(iv) is characteristic of a first-order trimethyl phosphate exchange process typified by rate law (3). This rate law is consistent with either a dissociative trimethyl phosphate exchange mechanism,

$$\text{Rate} = 4k_{ex}[\text{Be}\{(\text{MeO})_3\text{PO}\}_4{}^{2+}] \qquad (3)$$

or with exchange occurring in $[Be\{(MeO)_3PO\}_4]^{2+}$ exclusively solvated by trimethyl phosphate through either an associative or dissociative process. In solutions (i)—(iii) there are four trimethyl phosphate molecules available to solvate each $[Be\{(MeO)_3PO\}_4]^{2+}$ ion, whilst in solution (iv) there are nine such molecules available. Space-filling models indicate that up to ten trimethyl phosphate molecules are required to solvate $[Be\{(MeO)_3PO\}_4]^{2+}$, thus the close similarity of the kinetic parameters derived from solutions (iii) and (iv) argue against kinetically significant preferential solvation. Further evidence against preferential solvation may be adduced from the fact that preferential solvation of the complex $[Ni(dmso)_6]^{2+}$ by dmso (dmso = dimethyl sulphoxide) in the presence of nitromethane and methylene chloride diluents {and where the ratio: $[Ni(dmso)_6{}^{2+}]/[dmso]_{total}$ was much less than the analogous ratio in the trimethyl phosphate system} was shown not to be significant.[6] The observed rate law (3) is consequently considered to be symptomatic of a dissociative trimethyl phosphate exchange mechanism.

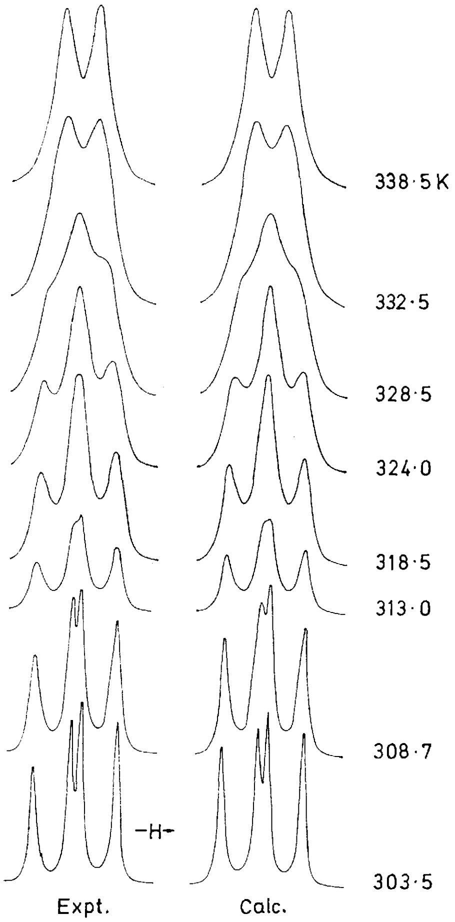

FIGURE 1 Experimental and calculated ^1H n.m.r. spectra arising from co-ordinated and bulk trimethyl phosphate in a solution in which $[Be^{2+}]$, $[(MeO)_3PO]_{total}$, and $[CH_2Cl_2]$ were respectively 0·124, 1·007, and 13·283M. The low-field doublet arises from co-ordinated trimethyl phosphate. The spectral amplitude scale is not constant

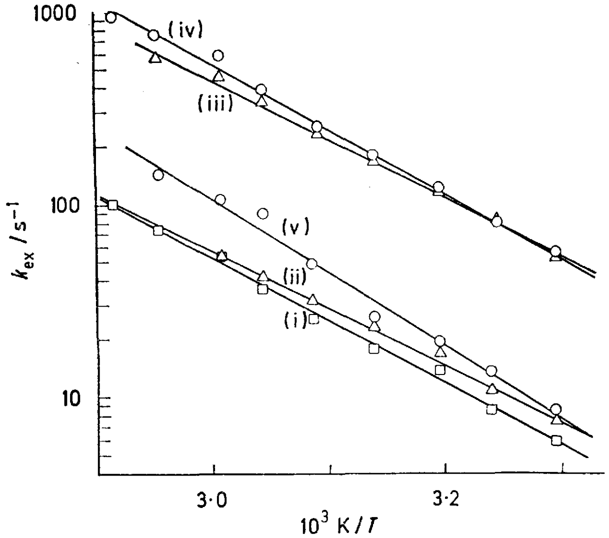

FIGURE 2 Semilogarithmic plot of k_{ex} data from the $[Be\{(MeO)_3PO\}_4]^{2+}$ system. Each best-fit line is labelled with the number of the solution to which it refers. (□), k_{ex} datum points from solution (i); (△), from solutions (ii) and (iii) ($10k_{ex}$); (○), from solutions (iv) ($10k_{ex}$) and (v)

From a consideration of the modes of simultaneous vibration of the four Be–O bonds in $[Be\{(MeO)_3PO\}_4]^{2+}$,

Rate and solution-composition data for beryllium(II) solvent-exchange systems

Solution	$[Be^{2+}]$ M	$[(MeO)_3PO]_{total}$ M	$[CH_2Cl_2]$ M	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}	k_{ex} (298 K) s^{-1}	Co-ordination number (263 K)	$\Delta G^‡$ (298 K) kJ mol^{-1}
(i)	0·543	4·430	6·301	59·4 ± 4·2	−34·7 ± 12·0	3·7 ± 0·7	4·1 ± 0·2	69·8
(ii)	0·338	2·740	8·674	54·4 ± 3·3	−49·4 ± 10·0	5·1 ± 0·6	3·9 ± 0·2	69·1
(iii)	0·124	1·007	13·283	56·9 ± 4·2	−43·9 ± 12·6	3·6 ± 0·6	4·0 ± 0·2	69·9
(iv)	0·121	1·624	12·130	61·9 ± 4·6	−26·8 ± 13·0	3·4 ± 0·8	4·1 ± 0·2	70·0
(v)	0·670	7·991		70·3 ± 8·4	3·5 ± 24·6	4·9 ± 1·8	4·0 ± 0·2	69·2
$[Be(dmf)_4]^{2+}$ system (ref. 9)				61·1 ± 1·3	10·9 ± 4·2	310	4	
$[Be(acac)(dmf)_2]^+$ system (ref. 9)				58·2 ± 2·4	−25·1 ± 8·4	22	2 (for dmf)	
$[Be(H_2O)_4]^{2+}$ system (ref. 8)						*ca.* 300	4	

Chemical shifts (±0·2 Hz) between co-ordinated and bulk trimethyl phosphate are respectively 15·4, 14·7, 13·5, 14·1, and 17·6 Hz for solutions (i)—(v) at 263 K. $J_{(^{31}P-^{1}H)}$ for co-ordinated trimethyl phosphate is 11·3 ± 0·2 Hz, and for bulk trimethyl phosphate 11·2 ± 0·2 Hz. dmf = Dimethylformamide and acac = acetylacetonato.

it appears that elongation of one Be–O bond simultaneously with the movement of beryllium(II) into the plane of the other three co-ordinating oxygen atoms is most likely to produce a trigonal-planar dissociative transition state for trimethyl phosphate exchange. Electrostatic calculations by Strehlow and Knoche,[14] however, show that formation of a trigonal-planar transition state for the $[Be(H_2O)_4]^{2+}$ system, although requiring a smaller $\Delta H^\ddagger$ value than a trigonal-pyramidal transition state, still requires a $\Delta H^\ddagger$ value only slightly less than the Be–O bond energy (*ca.* 400 kJ mol^{-1}). A $\Delta H^\ddagger$ value similar to that observed for water substitution is only obtained when a water molecule is sited on each face of the trigonal-planar transition state (the Be–O distance of closest approach for a water molecule on the trigonal face is *ca.* 28% greater than the Be–O distance in the trigonal plane). As essentially the same predominant electrostatic and steric interactions between beryllium(II) and the solvent oxygen atoms occur in the trimethyl phosphate and aqueous systems, electrostatic energies for the model transition states will be similar for both systems. On this basis solvent-exchange mechanisms must be viewed as solvent-assisted dissociative processes.

Although the electrostatic model rationalises the major enthalpic aspects of the dissociative mechanism, calculations become less precise as ligand complexity increases; also it is difficult to account for solvent interactions outside the first co-ordination sphere other than in terms of a continuum model, and, as a consequence, variations of observed $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values from system to system (see Table) are not readily explained. Qualitatively interaction of the beryllium(II) complex with solvent outside the first co-ordination sphere is expected to be dependent on the geometry and charge density of the first co-ordination sphere, and the bulk characteristics of the solvent itself. The charge density is expected to depend on the size of the co-ordinated solvent molecule and its electron-donating characteristics, which, to some extent, determine the energy of the primary bond-breaking process. Thus a considerable inter-relation of the possible sources of contributions to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ may occur.

Bennetto and Caldin[3] have proposed a dissociative model, consistent with the linear correlation observed between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for solvent exchange and ligand substitution on several bivalent metal ions in a range of solvents, in which contributions to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ arising from solvent interactions outside the first co-ordination sphere are considered. According to this model the elongation of a beryllium(II)–trimethyl phosphate bond sufficient to overcome the bonding interaction (process 3 in the nomenclature of ref. 3) is characterised by $\Delta H^\ddagger[Be\{(MeO)_3PO\}_4{}^{2+}]$, but the movement of the outgoing trimethyl phosphate molecule is not sufficient for $\Delta S^\ddagger[Be\{(MeO)_3PO\}_4{}^{2+}]$ to be significant (a concerted rearrangement of the remaining three trimethyl phosphate ligands, as previously discussed, is also envisaged as part of process 3). In dilute solution, solvent in the immediate vicinity (region B) of the complex $[Be\{(MeO)_3PO\}_4]^{2+}$ is considered to be in a state of high entropy, whereas the more distant solvent (region C) is relatively ordered. If nett transfer of solvent from region B to C is synchronous with process 3 in the activation process, a decrease in entropy occurs ($\Delta S_{\text{struct}}{}^\ddagger$ in the nomenclature of ref. 3) and $\Delta S^\ddagger$ is negative as a result. If this process is considered analogous to a condensation process, a negative $\Delta H_{\text{struct}}{}^\ddagger$ contribution to $\Delta H^\ddagger$ is expected. The signs of $\Delta S_{\text{struct}}{}^\ddagger$ and $\Delta H_{\text{struct}}{}^\ddagger$ are reversed if nett solvent transfer in the opposite direction occurs. The former case fits the data for exchange of trimethyl phosphate in $[Be\{(MeO)_3PO\}_4]^{2+}$ in the presence of methylene chloride, but it should be noted that in the most concentrated solutions it seems improbable that region C will exist to a significant extent. Nevertheless the model provides a convenient method of identifying contributions to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ apparently arising from processes thermodynamically analogous to those envisaged in dilute solution.

In the absence of methylene chloride, the activation parameters for trimethyl phosphate exchange, despite the substantial experimental error, appear to differ significantly from those observed in the presence of the diluent ($\Delta G^\ddagger$ values for all five solutions are very similar, however). In this system [solution (v)] the paucity of solvent is such that free trimethyl phosphate molecules are in contact with the first co-ordination sphere of the complex $[Be\{(MeO)_3PO\}_4]^{2+}$ and with ClO_4^-, also, in most cases. Under these circumstances the solute may well determine the thermodynamics of solvent interactions to a significant extent, but the introduction of methylene chloride [solutions (i)—(iv)] appears to modify this apparent solute effect.

Interpretation of the data for the two dimethylformamide (dmf) systems in terms of the above model, suggests that the transition states arising from the complexes $[Be(dmf)_4]^{2+}$ and $[Be(acac)(dmf)_2]^+$ (acac = acetylacetonato) interact differently with their environment, as might be expected from nett charge and geometric considerations. The data in the Table are consistent[3] with $\Delta H^\ddagger[Be\{(MeO)_3PO\}_4{}^{2+}]$ {and $\Delta H^\ddagger$-$[Be(dmf)_4{}^{2+}]$} average values of *ca.* 64 kJ mol^{-1}, which compare with values, for the analogous quantities, of *ca.* 48 and *ca.* 38 kJ mol^{-1} for the exchange of oxygen-donor solvents on magnesium(II),[11] and for ligand substitution and solvent exchange on eight bivalent metal ions in oxygen- and nitrogen-donor solvents.[3] The relatively high beryllium(II) value is attributable to the high surface charge density of that ion.

EXPERIMENTAL

Preparation of Tetrakis(trimethyl phosphato)beryllium(II) *Perchlorate*, $[Be\{(MeO)_3PO\}_4](ClO_4)_2$.—A solution of hydrated $Be(ClO_4)_2$ in an excess of redistilled trimethyl phosphate was prepared. Water was removed from this solution by agitation (24 h) over a bed of Linde 4A molecular

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[14] H. Strehlow and W. Knoche, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 427.

sieves, calculated to be sufficient to remove the amount of water in solution many times over. The solution was filtered off and the dehydration process was repeated twice prior to filtering and reducing the solution volume on a vacuum line, whereupon colourless $[Be\{(MeO)_3PO\}_4](ClO_4)_2$ crystals precipitated. These crystals were twice recrystallised by dissolution in dry methylene chloride, followed by reprecipitation on addition of dry diethyl ether. The crystals were washed with dry diethyl ether and dried *in vacuo* (40%) (Found: C, 18·65; H, 4·70; Be, 1·20; P, 16·0. $[Be\{(MeO)_3PO\}_4](ClO_4)_2$ requires C, 18·75; H, 4·70; Be, 1·15; P, 16·1%). Analyses for C, H, and P were performed by the Australian Microanalytical Service, Melbourne, and Be^{2+} analyses were performed using an ion-exchange technique.[15]

Proton Magnetic Resonance Measurements.—All solutions were made up in redistilled trimethyl phosphate and CH_2Cl_2 (dried and stored over Linde 4A molecular sieves) by weight under a dry-nitrogen atmosphere, and were sealed under vacuum in standard n.m.r. tubes, each of which contained a sealed Me_4Si capillary to provide a lock signal. Solution densities were determined using a Lang–Levy pipette. All spectra were run in triplicate on a Varian DA-60-IL spectrometer thermostatted to ±0·5 K.

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[15] A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, Green, and Co., London, 1961, p. 702.