Enthalpies of Solution of Triphenyl Derivatives of the Group 5 Elements †

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Enthalpies of solution of the compounds MPh_3 (M = N, P, As, Sb, or CH) and Ph_2O in methanol and in acetonitrile are reported; the solubility of PPh_3 in a range of solvents is described.

THERE is very little information published pertaining to the solubilities and enthalpies and entropies of solution of triphenylphosphine or of other analogous Group 5 bases in organic solvents. This situation exists despite the importance of equilibrium loss of PPh_3 (or similar bases) from such complexes as $[Pt(PPh_3)_{3\text{ or }4}]$, $[RhCl(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, or $[Pt(C_2Cl_4)(PPh_3)_2]$ in homogeneous catalysis [1] or isomerisation reactions.[2] An enthalpy of solution for PPh_3 in ethanol of +5.49 kcal mol^{-1} has been reported.[3,‡] We have therefore determined these quantities for the dissolution of triphenylphosphine in methanol, ethanol, acetonitrile, and benzene. We have also determined the enthalpies of solution of other compounds MPh_3, where M = N, As, Sb, or CH, and of Ph_2O, in methanol and in acetonitrile, to see how these enthalpies vary within Group 5 and between Group 5 and adjacent elements of the Periodic Table.

TABLE 1

Enthalpies of solution (kJ mol^{-1}) of compounds MPh_3 (M = N, P, As, Sb, or CH) and of Ph_2O in various solvents (at 298.2 K). The error limits stated are the standard errors of the means. The number of independent determinations was six except where indicated otherwise

Solvent Compd.	MeOH	MeCN	C_6H_6	EtOH
NPh_3	24.5 ± 0.6	27.8 ± 0.5		
PPh_3	23.2 ± 0.4	27.5 ± 0.7	15.9 ± 0.3 [a]	22.7 ± 0.4 [b,c]
$AsPh_3$	23.2 ± 0.3	26.4 ± 0.2		
$SbPh_3$	26.7 ± 0.7	27.7 ± 0.1		
Ph_3CH	25.1 ± 0.2	26.1 ± 0.5		
Ph_2O	21.4 ± 0.3	22.5 ± 0.4		

[a] Four determinations. [b] Eight determinations. [c] Compare the value of $22.9_7 \pm 0.0_4$ kJ mol^{-1} of ref. 3.

TABLE 2

Solubilities and free energies and entropies of solution [a] of triphenylphosphine in various solvents at 298.2 K

Solvent	MeOH	MeCN	C_6H_6	EtOH	C_6H_{12}	Dioxan	Tetra-hydrofuran
Solubility/mol dm^{-3}	0.08	0.31	13.0	0.18	1.26	2.0	2.5
Method used	*b*	*b*	*c*	*b*	*d*	*c*	*c*
$\Delta G^{\ominus}$ (solution)/kJ mol^{-1}	+6.2	+2.9	−6.3	+4.2			
$\Delta S^{\ominus}$ (solution)/J K^{-1} mol^{-1}	+57	+82	+75	+62			

[a] The standard state here is the hypothetical ideal solution of unit molarity. [b] Spectrophotometric with approximate gravimetric check. [c] Gravimetric. [d] Spectrophotometric.

EXPERIMENTAL

The compounds used were of the best available commercial grade, recrystallised where necessary until conforming to published melting points. Solvents were purified and dried by conventional methods; methanol was distilled from magnesium and iodine, ethanol dried over calcium oxide, and acetonitrile dried over anhydrous calcium sulphate.

Enthalpies of solution were determined in an LKB 8700 precision calorimeter. This was connected to a Wheatstone bridge circuit, constructed in these laboratories, employing a Kipp-Zonen BD5 recorder as monitor. The performance of this apparatus was checked periodically against the well-established enthalpies of solution of potassium chloride [4] or of neutralisation of tris(hydroxymethyl)methylamine.[5]

Solubilities were estimated either by direct weighing of residues from complete evaporation of aliquots of saturated solutions or spectrophotometrically.

RESULTS AND DISCUSSION

Mean values for the measured enthalpies of solution are reported, with the standard errors of their means, in Table 1. Solubilities of PPh_3 in several solvents are reported in Table 2. This Table also includes values for the entropies of solution of PPh_3 calculated from Table 1 *via* the free energies of solution stated; activity coefficients of unity were assumed in estimating these free energies.

There is a reasonably regular pattern for the enthalpies of solution of compounds MPh_3 (M = N, P, As, Sb, or CH) in methanol and in acetonitrile. However, it is difficult to rationalise satisfactorily the variation in solubilities or entropies of solution of PPh_3 in the range of solvents studied. Attempts to correlate these values with such empirical solvent parameters as Reichardt's spectroscopically based E_T values [6] or Hildebrand and

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† No reprints available.

‡ 1 cal = 4.184 J.

[1] See, for example, G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, 'Principles of Organometallic Chemistry,' Methuen, London, 1968, ch. 10; B. R. James and L. D. Markham, *Inorg. Chem.*, 1974, **13**, 97; K. G. Caulton, *J. Amer. Chem. Soc.*, 1974, **96**, 3005.

[2] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **15**, 217.

[3] G. Beech, S. J. Ashcroft, and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1967, 929.

[4] V. B. Parker, 'Thermal Properties of Aqueous Uni-univalent Electrolytes,' U.S. Department of Commerce, NSRDS-NBS **2**, 1965, table 18.

[5] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 1964, **18**, 195; J. O. Hill, G. Ojelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111; E. J. Prosen and M. V. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, **A77**, 581.

[6] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1.

Scott's ' solubility parameter of the solvent '[7] met with little success. Nonetheless the high solubility of PPh_3 in benzene is at least consistent with the apparently greater ease of reversible loss of this ligand from some of the compounds cited in the Introduction.

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[7] J. H. Hildebrand and R. L. Scott, ' The Solubility of Non-electrolytes,' 3rd edn., Dover Publications, New York, 1964, ch. 17; ' Regular Solutions,' Prentice-Hall, New Jersey, ch. 9 and appendix 5.