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Thermochemical studies on the halogenation of tetraphenyllead

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Reliable thermochemical data for organolead compounds are restricted to the standard enthalpies of formation of tetramethyl- and tetraethyllead[1]. We report the results of studies on the bromination and iodination of tetraphenyllead and the corresponding triphenyllead halides.

$$Ph_4Pb + 2X_2 \rightarrow Ph_2PbX_2 + 2PhX \text{ } (CHCl_3 \text{ solution}) \quad (1)$$

$$Ph_3PbX + X_2 \rightarrow Ph_2PbX_2 + PhX \text{ } (CHCl_3 \text{ solution}) \quad (2)$$

(X = Br or I)

Measurements were made using an LKB reaction calorimeter and the completeness of reaction was checked by volumetric analysis and thin layer chromatography[2].

The results are shown in Table 1 where 1 calorie = 4.184 abs. J and the uncertainties are twice the standard deviation of the mean. The enthalpies of formation of the crystalline solids are shown in Table 2. They have been calculated by making use of the subsidiary data[3] ΔH_f° (PhBr, 1) = 14.5 ± 1.0 kcal·mole^{-1}, ΔH_f° (PhI, 1) = 27.7 ± 0.7 kcal·mole^{-1} together with the relevant enthalpies of solution. The value 122 kcal·mole^{-1} has been used for the standard enthalpy of formation of crystalline tetraphenyllead. This is based on the bond energy scheme for the Group IV organometallic compounds which we have described elsewhere[4]. We hope shortly to obtain a direct calorimetric estimate of this quantity from work which is being carried out at present in the rotating aneroid combustion calorimeter described previously[5].

TABLE 1

ENTHALPIES FOR REACTION IN $CHCl_3$ SOLUTION

X	Reaction (1)		Reaction (2)	
	Br	I	Br	I
$-\Delta H$ kcal·mole^{-1}	86.55±0.65	32.57±0.30	40.86±0.46	14.16±0.09

TABLE 2

STANDARD ENTHALPIES OF FORMATION

	Ph_3PbBr	Ph_2PbBr_2	Ph_3PbI	Ph_2PbI_2
ΔH_f°, c, kcal·mole^{-1}	64.6±2.0	8.2±1.6	76.9(5)±1.3	35.3(5)±1.1

REFERENCES

1 D.W. Scott, W.D. Good and G. Waddington, *J. Phys. Chem.*, 60 (1956) 1090.
2 A.W. Krebs and M.C. Henry, *J. Org. Chem.*, 28 (1963) 1911.
3 J.D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970.
4 A.S. Carson, P.G. Laye, J.A. Spence and W.V. Steele, *J. Chem. Thermodynamics*, in press.
5 G.P. Adams, A.S. Carson and P.G. Laye, *Trans. Faraday Soc.*, 65 (1969) 113.