

Preliminary communication

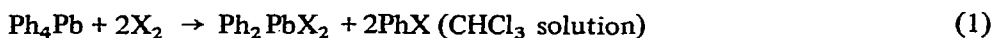
Thermochemical studies on the halogenation of tetraphenyllead

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Reliable thermochemical data for organolead compounds are restricted to the standard enthalpies of formation of tetramethyl- and tetraethyllead¹. We report the results of studies on the bromination and iodination of tetraphenyllead and the corresponding triphenyllead halides.



(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 chromatography².

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 data³ $\Delta H_f^\circ(\text{PhBr}, 1) = 14.5 \pm 1.0 \text{ kcal}\cdot\text{mole}^{-1}$, $\Delta H_f^\circ(\text{PhI}, 1) = 27.7 \pm 0.7 \text{ kcal}\cdot\text{mole}^{-1}$ together with the relevant enthalpies of solution. The value $122 \text{ kcal}\cdot\text{mole}^{-1}$ 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 elsewhere⁴. 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 previously⁵.

TABLE 1

ENTHALPIES FOR REACTION IN CHCl₃ SOLUTION

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

TABLE 2

STANDARD ENTHALPIES OF FORMATION

	Ph ₃ PbBr	Ph ₂ PbBr ₂	Ph ₃ PbI	Ph ₂ PbI 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

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