636. *The Thermochemistry of Organo-arsenic Compounds. Part III.* Phenylarsine.*

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The heat of reaction at 25° of liquid phenylarsine with iodine (dissolved in carbon tetrachloride) to yield a solution of phenylarsenic di-iodide and hydrogen iodide has been measured: $\Delta H_{\text{obs.}} = -31{\cdot}0 \pm 1$ kcal./mole. From this, one may derive $\Delta Hf°$ ($PhAsH_2$, liq.) $-$ $\Delta Hf°$ ($PhAsI_2$, liq.) $= 22{\cdot}9 \pm 1{\cdot}7$ kcal./mole.

The *difference* between the mean bond-dissociation energies of the As–H and As–I bonds in phenylarsine and in phenylarsenic di-iodide is obtained ($\Delta\bar{D} = 17{\cdot}0 \pm 2{\cdot}3$ kcal./mole), and is very close to the corresponding difference between the bonds in arsine and in arsenic tri-iodide.

ACCORDING to Blicke and Powers (*J. Amer. Chem. Soc.*, 1933, **55**, 1161), one mol. of phenylarsine, dissolved in ether, reacts instantly with two mols. of iodine to give a quantitative yield of phenylarsenic di-iodide:

$$PhAsH_2 + 2I_2 \longrightarrow PhAsI_2 + 2HI \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The same reaction—to the extent of at least 98%—was observed in benzene as solvent.

The quantitative nature, and the rapidity, of reaction (1) made it seem probable that the reaction might be amenable to thermal study, but several difficulties were encountered before we developed a satisfactory method of handling the reaction in a calorimeter. These difficulties arise from (i) the extreme reactivity of phenylarsine, particularly towards oxygen and oxidants, thus necessitating an inert atmosphere, and a dry solvent of high purity, and (ii) the generally low solubility of hydrogen iodide in inert solvents. Pyridine appeared likely to be a satisfactory solvent, in that it readily absorbs hydrogen iodide, and several experiments were carried out in that solvent. However, a satisfactory reproducibility in the thermal results was not attained; this may be due to the well-known difficulty of obtaining pyridine in a pure dry state. Some reactions in methanol suggested that the reaction in this solvent does not follow eqn. (1) and that the methanol enters into reaction at some stage of the iodination. The uptake of iodine by phenylarsine in methanol was found to be less than required by the reaction (1), and experiments using this solvent were abandoned.

Satisfactorily reproducible results were obtained by using pure dry carbon tetrachloride as solvent. From blank experiments outside the calorimeter it was found that the reaction in carbon tetrachloride proceeds to at least 98% completion according to eqn. (1).

EXPERIMENTAL

Preparation of Compounds.—Phenylarsine was prepared by reduction of phenylarsonic acid, as described by Palmer and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 1356), *viz.*:

$$PhAsO(OH)_2 + 3H_2 \longrightarrow PhAsH_2 + 3H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The reduction was carried out in ethereal solution with zinc dust and concentrated hydrochloric acid. The ethereal layer was separated, washed with dilute aqueous sodium hydrogen carbonate, and dried ($CaCl_2$). All operations were performed in an inert atmosphere. The product was separated from the ether by distillation and, purified by fractional distillation through a 6″ steel-gauze packed column, had b. p. 44·8—45·0°/5·5 mm. The pure product was finally distilled in a high vacuum and collected and sealed in thin, weighed, glass ampoules. Phenylarsenic di-iodide was prepared by Steinkopf and Smie's method (*Ber.*, 1926, **59**, 1461). The crude oil was purified by recrystallization from cooled alcohol.

Carbon tetrachloride of " AnalaR " (medicinal) grade was degassed, saturated with nitrogen, and dried ($CaCl_2$) before use in the calorimeter.

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* Part II, *J.*, 1953, 1181.

Calorimeter.—The calorimeter has been described by Mortimer and Skinner (*J.*, 1952, 4331). The experiments were performed by breaking the ampoules containing known amounts of phenylarsine under the surface of 750 c.c. of carbon tetrachloride (containing dissolved iodine) in the Dewar vessel. An excess of iodine—normally 10% excess on the requirement of eqn. (1)—was used to assist completion of the reaction. The whole Dewar assembly was flushed with pure dry nitrogen before the experiments were started, and a slow steady stream of nitrogen was maintained in the head-piece of the Dewar calorimeter throughout each run. Temperature changes were followed by the resistance change in a shielded thermistor element immersed in the reaction solution. The calorimeter was calibrated electrically by the substitution method.

Units.—All heat quantities are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. joule. The reactions were performed at 25°.

Results.—The observed heat of reaction, $\Delta H_{\text{obs.}}$, refers to the system

$$\text{PhAsH}_2\text{(liq.)} + 2\text{I}_2(\text{CCl}_4 \text{ soln.}) \longrightarrow \{\text{PhAsI}_2 + 2\text{HI}\} (\text{CCl}_4 \text{ soln.}) \quad . \quad . \quad . \quad . \quad (3)$$

From six experiments, with quantities of phenylarsine in the range 0·4—0·6 g., and 10% excess of iodine in each case, the mean value $\Delta H_{\text{obs.}} = -31{\cdot}0$ kcal./mole was obtained, subject to a possible error of ± 1 kcal./mole.

$\Delta H_{\text{obs.}}$ incorporates the heat terms arising from the solution of iodine, phenylarsenic di-iodide, and hydrogen iodide in carbon tetrachloride. Hartley and Skinner (*Trans. Faraday Soc.*, 1950, **46**, 621) have reported $\Delta H_{\text{soln.}}$ (I_2, CCl_4) = 5·8 ± 0·2 kcal./mole, and their value is used here. The heat of solution of gaseous hydrogen iodide in carbon tetrachloride was measured directly, $\Delta H_{\text{soln.}}$ (HI, CCl_4) = $-4{\cdot}9 \pm 0{\cdot}1$ kcal./mole. The heat of solution of phenylarsenic di-iodide in carbon tetrachloride containing iodine * (equivalent in amount to the excess of iodine remaining in solution on completion of the reaction) was measured independently: $\Delta H_{\text{soln.}}(\text{PhAsI}_2, \text{CCl}_4) = 0{\cdot}9 \pm 0{\cdot}05$ kcal./mole. For the idealized reaction:

$$\text{PhAsH}_2\text{(liq.)} + 2\text{I}_2 \text{ (cryst.)} \longrightarrow \text{PhAsI}_2\text{(liq.)} + 2\text{HI (g.)} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

one may then derive $\Delta H = -10{\cdot}5 \pm 1{\cdot}7$ kcal./mole. From this, and the value $\Delta Hf°$ (HI, g.) = 6·20 kcal./mole (Nat. Bur. Stand. Circular 500, 1952), it follows that

$$\Delta Hf°(\text{PhAsH}_2, \text{liq.}) - \Delta Hf°(\text{PhAsI}_2, \text{liq.}) = 22{\cdot}9 \pm 1{\cdot}7 \text{ kcal./mole} \quad . \quad . \quad . \quad . \quad (5)$$

DISCUSSION

Equation (5) serves as a starting-point from which the difference between the As–H and As–I bond energies in these compounds may be derived. We use the symbol $\bar{D}$(As–H) to represent the *mean* bond dissociation energy of the As–H bonds in phenylarsine, where $\bar{D}$(As–H) is defined from

$$\text{PhAsH}_2 \text{ (g.)} \longrightarrow \text{PhAs (g.)} + 2\text{H (g.)}; \ \Delta H = 2\bar{D}(\text{As–H}) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Correspondingly, $\bar{D}$(As–I) in phenylarsenic di-iodide is defined from

$$\text{PhAsI}_2 \text{ (g.)} \longrightarrow \text{PhAs (g.)} + 2\text{I (g.)}; \ \Delta H = 2\bar{D}(\text{As–I}) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By combining eqns. (6) and (7), and using the well-established values $\Delta Hf°$ (H, g.) = 52·1 and $\Delta Hf°$ (I, g.) = 25·5 kcal./mole (N.B.S. Circular 500), one can express the difference between $\bar{D}$(As–H) and $\bar{D}$(As–I) by the equation

$$\Delta\bar{D}\begin{bmatrix}\text{As–H}\\ \text{As–I}\end{bmatrix} = 26{\cdot}6 + \tfrac{1}{2}\Delta Hf° \text{ (PhAsI}_2\text{, g.)} - \tfrac{1}{2}\Delta Hf°(\text{PhAsH}_2\text{, g.}) \quad . \quad . \quad . \quad . \quad (8)$$

Equation (5) enables us to eliminate the terms in $\Delta Hf°$ from eqn. (8), and obtain

$$\Delta\bar{D}\begin{bmatrix}\text{As–H}\\ \text{As–I}\end{bmatrix} = 15{\cdot}1 \ (\pm 0{\cdot}8) + \tfrac{1}{2}(\lambda_1 - \lambda_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $\lambda_1 = -\Delta H_{\text{vap.}}(\text{PhAsI}_2)$ and $\lambda_2 = -\Delta H_{\text{vap.}}(\text{PhAsH}_2)$. The value of λ_2 may be estimated at 12·7 ± 1 kcal./mole from our own and other vapour-pressure data quoted by

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* There is a small heat of mixing of phenylarsenic di-iodide with dissolved iodine. The heat of solution of phenylarsenic di-iodide in pure carbon tetrachloride alone was measured as: $\Delta H_{\text{soln.}} = 1{\cdot}64 \pm 0{\cdot}05$ kcal./mole.

Goddard (Newton-Friend's "Textbook of Inorganic Chemistry," Vol. II, Part 2, 1930, p. 63, Griffin & Co. Ltd.). The vapour-pressure data on phenylarsenic di-iodide are too scanty to allow a direct estimate of λ_1, but a rough value may be got as follows; from Redemann, Chaikin, Fearing, and Benedict's vapour-pressure data (*J. Amer. Chem. Soc.*, 1948, **70**, 637) on phenylarsenic dichloride, the latent heat of vaporization may be calculated: $\lambda_{\text{vap.}}(\text{PhAsCl}_2) = 13{\cdot}9$ kcal./mole. This corresponds to a value of 26·6 for the Trouton constant, and if we now carry this over to the case of phenylarsenic di-iodide, we then obtain $\lambda_1 \cong 16{\cdot}4$ kcal./mole. After allowance for a possible error of ± 2 kcal./mole in this estimate of λ_1, eqn. (9) becomes

$$\Delta\bar{D}\begin{bmatrix}\text{As–H}\\ \text{As–I}\end{bmatrix} = 17{\cdot}0 \pm 2{\cdot}3 \text{ kcal./mole} \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

Mortimer and Skinner (*J.*, 1952, 4331) have given values for the mean bond-dissociation energy in arsine, $\bar{D}(\text{As–H}) = 58{\cdot}6$ kcal./mole, and in arsenic tri-iodide, $\bar{D}(\text{As–I}) = 42{\cdot}6$ kcal./mole, from which the difference $\Delta\bar{D}\begin{bmatrix}\text{As–H}\\ \text{As–I}\end{bmatrix} = 16{\cdot}0$ kcal./mole results, in close agreement with the corresponding value of $\Delta\bar{D}$ given in eqn. (10).

We shall describe the molecule phenylarsine as a " mixed " molecule, derived from the " parent " molecules arsine and triphenylarsine; similarly, the parents of phenylarsenic di-iodide are arsenic tri-iodide and triphenylarsine. A general thermochemical problem of mixed molecules may now be formulated : how far can values appropriate to the parents be carried over unchanged to the mixed molecule? The present investigation suggests that in the mixed molecules PhAsX_2 the values $\bar{D}(\text{As–X})$ are transferable from the parents AsX_3.

From measurements of the heats of reaction of diphenylmercury with the mercuric halides, Hartley, Pritchard, and Skinner (*Trans. Faraday Soc.*, 1951, **47**, 254) concluded that the $\bar{D}$ values in phenylmeruric iodide are, within small error limits, transferable from the parents. In phenylmercuric bromide and chloride, the $\bar{D}$ values are enhanced by a few kcal./mole above the parent values. In the alkylmercuric halides, RHgX (R = Me, Et, Pr, Pr^i), the $\bar{D}$ values are enhanced appreciably over the parent values.

Mortimer and Skinner (*loc. cit.*) obtained a value for $\bar{D}(\text{As–I})$ in cacodyl iodide, which is higher by 4—6 kcal./mole than $\bar{D}(\text{As–I})$ in arsenic tri-iodide. Skinner and Tees (*J.*, in the press), from studies on the dibutylboron halides, expressed the view that in these compounds the $\bar{D}(\text{B–Bu})$ values are enhanced over the parent value. The evidence at present suggests that, in the mixed compounds of the general type R_nMX_m, where M is the $(n + m)$-valent central atom, the $\bar{D}$ values are transferable from the parents when R = Ph and X = H or I, but that enhancement occurs in one or more of the $\bar{D}$ values when R = alkyl and X = halogen.

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