828. *The Thermochemistry of Organo-arsenic Compounds. Part I. Cacodyl,* As_2Me_4.

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The heat of reaction of liquid cacodyl with iodine in methanol solution has been measured at 25° ($\Delta H_{\text{corr.}} = -19{\cdot}9 \pm 0{\cdot}2$ kcal. mole^{-1}), from which the relationship $\Delta Hf°(\text{Me}_2\text{AsI, liq.}) = \frac{1}{2}\Delta Hf°(\text{Me}_4\text{As}_2\text{, liq.}) - 9{\cdot}96$ kcal. is derived. From this a further relationship is got between the dissociation energy of the As–I bond in Me_2AsI (D_1), and the As–As bond in Me_4As_2 (D_2), *viz.*: $(D_1 - \frac{1}{2}D_2) = 29{\cdot}8 \pm 1{\cdot}5$ kcal. mole^{-1}. Some general considerations on the value of D_2 lead to the conclusion that D_1 probably lies within the range 47—50 kcal. mole^{-1}.

TETRAMETHYLDIARSINE (cacodyl) is highly reactive, spontaneously inflammable in air, and readily split at the As–As bond by halogens to give the secondary halides, Me_2AsX (see, *e.g.*, Sidgwick, " Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 770). We have found that the reaction of cacodyl with iodine in methanol solution occurs rapidly at room temperature, and is suitable for thermochemical study. The heat of iodination represents, however, only a limited contribution to the thermochemistry of cacodyl and cacodyl iodide, giving merely the difference in heat content of the two substances. An attempt to supplement the information reported here by study of the controlled oxidation of cacodyl was not successful (owing to the complexity of the reaction), and the discussion of the present work is not as complete as we would otherwise have desired.

EXPERIMENTAL

Materials.—Cacodyl was prepared by Auger's method (*Compt. rend.*, 1906, **142**, 1153) by reducing cacodylic acid with hypophosphorous acid. The crude product was dried ($CaCl_2$) and distilled under a reduced pressure of nitrogen through a 6″ gauze-packed column. The fraction collected over the range 43·8—44·3°/11 mm. was redistilled *in vacuo* and sealed in thin weighed glass phials.

Cacodyl iodide was prepared from cacodylic acid by Burrows and Turner's method (*J.*, 1920, 1376) and purified by fractional distillation (b. p. 43·3—43·4°/10·5 mm.).

The methanol was a high-grade synthetic product, and the iodine was " AnalaR."

Calorimeter.—This was a narrow-necked 1-l. Dewar vessel, similar to that described by Charnley, Skinner, and Smith (*J.*, 1952, 2288), except that the tube-breaking platform and supports were of glass, and an inlet (for nitrogen) was let into the stopper in the neck of the Dewar flask. Temperature changes were recorded in terms of the resistance change of a thermistor element. The calorimeter was calibrated electrically by the substitution method.

RESULTS

The iodination reaction was studied by breaking phials containing weighed amounts of cacodyl into a solution of iodine in methanol (750 c.c.) contained in the Dewar vessel. Normally, a small excess of iodine relative to cacodyl was used, but in some experiments this ratio was reversed. Preliminary experiments demonstrated the need to avoid the complications that might arise from oxidation of cacodyl. Accordingly, the air-space above the solution in the Dewar vessel was thoroughly swept out with nitrogen both before and during each experiment. Before the iodine solutions were made up, the methanol was alternately degassed and saturated with nitrogen until rid of all dissolved oxygen. These precautions proved to be sufficient, and we were able successfully with this technique to measure the negative heat of solution of cacodyl in methanol.

The observed heats of reaction (listed under $\Delta H_{\text{obs.}}$ in Table 1) refer to the equation :

$$\text{Me}_2\text{As}{\cdot}\text{AsMe}_2\text{(liq.)} + (n+1)\text{I}_2\text{(soln.)} \longrightarrow \{2\text{Me}_2\text{AsI} + n\text{I}_2\}\text{(soln.)} \quad . \quad . \quad (1)$$

in which n is a small fraction, $< \pm 0{\cdot}1$. The values listed under $\Delta H_{\text{corr.}}$ refer to the heat of the idealized reaction,

$$\text{Me}_2\text{As}{\cdot}\text{AsMe}_2\text{(liq.)} + \text{I}_2\text{(cryst.)} \longrightarrow 2\text{Me}_2\text{AsI(liq.)} \quad . \quad . \quad . \quad . \quad (2)$$

and are derived from $\Delta H_{\text{obs.}}$ after correction for the various solution heats contained therein.

The heats of solution involved are:

(i) I_2(cryst.) in methanol, $\Delta H_{\text{soln.}} = 2{\cdot}07 \pm 0{\cdot}05$ kcal. mole^{-1} (Hartley and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 621).
(ii) As_2Me_4(liq.) in methanol, $\Delta H_{\text{soln.}} = 0{\cdot}85 \pm 0{\cdot}04$ kcal. mole^{-1}.
(iii) Me_2AsI(liq.) in methanol, $\Delta H_{\text{soln.}} = 1{\cdot}08 \pm 0{\cdot}03$ kcal. mole^{-1}.
(iv) Me_2AsI(liq.) in methanol–I_2 solutions.

The correction term (iv) was the subject of a separate study, results of which are summarized in Table 2.

TABLE 1. *Iodination of cacodyl.*

Expt.	Cacodyl (g.)	I_2 (g.)	n (Eqn. 1)	m (Eqn. 4)	$\Delta H_{\text{obs.}}$ (kcal. mole^{-1})	$\Delta H_{\text{corr.}}$ (kcal. mole^{-1})
1	1·3826	1·8283	0·094	0·047	−21·43	−19·96
2	1·2830	1·7746	0·144	0·072	−22·16	−19·85
3	1·8134	2·5175	0·148	0·074	−22·33	−19·96
4	1·3785	1·9059	0·144	0·072	−22·32	−20·01
5	1·3509	1·4745	−0·097	—	−19·72	−19·81

Mean: $\Delta H_{\text{corr.}} = -19{\cdot}92$ kcal. mole^{-1}.
Final value: $\Delta H_{\text{corr.}} = -19{\cdot}9 \pm 0{\cdot}2$ kcal. mole^{-1}.

TABLE 2. *Solution of cacodyl iodide in methanolic iodine.*

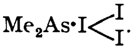
Expt.	Me_2AsI (g.)	I_2 * (g.)	m (Eqn. 4)	$\Delta H_{\text{obs.}}$ (kcal. mole^{-1})
1	3·3206	0·0000	0	1·08
2	3·3371	0·2610	0·071	− 0·12
3	3·1619	0·8370	0·242	− 2·40
4	3·4963	1·7254	0·452	− 5·03
5	3·0454	2·5551	0·767	− 8·44
6	3·1185	3·55	1·04	−11·16

* Dissolved in 750 c.c. of methanol.

We have observed that the brown colour of dissolved iodine is almost instantaneously destroyed when equimolar proportions of cacodyl and iodine are mixed. But disappearance of the iodine colour occurs even when an *excess* (up to *ca.* 50%) of iodine is used. In accord with this, the addition of dimethyliodoarsine, Me_2AsI, to iodine solutions was found to destroy the brown colour (provided the former is in considerable excess). This "secondary" reaction is presumably the addition:

$$Me_2AsI + I_2 \rightleftharpoons Me_2AsI_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

in which the adduct may contain quinquevalent arsenic, or alternatively is the tri-iodide



$Me_2As{\cdot}I\!<^{I}_{I}$.

To allow for the thermal effect of the secondary reaction in the experiments in which excess of iodine was used, a series of measurements on the heat of solution of iododimethylarsine in methanolic iodine was made. The values of $\Delta H_{\text{obs.}}$ in Table 2 refer to the reaction system:

$$Me_2AsI(\text{liq.}) + mI_2(\text{soln.}) \longrightarrow \text{Products(soln.)} \quad . \; . \; . \; . \; . \quad (4)$$

where the "products" may contain unchanged dimethyliodoarsine and iodine, as well as the tri-iodide Me_2AsI_3. It may be noted that the relationship between the factors m (in eqn. 4) and n (in eqn. 1) is simply $m = n/2$.

DISCUSSION

The heat of reaction (2) relates the heats of formation of cacodyl and cacodyl iodide from elements in their standard states [whence $\Delta Hf^{\circ}I_2(\text{cryst.}) = 0$] through the equation:

$$\Delta Hf^{\circ}(Me_2AsI, \text{liq.}) = \tfrac{1}{2}\Delta Hf^{\circ}(Me_4As_2, \text{liq.}) - 9{\cdot}96 \text{ kcal.} \quad . \; . \quad (5)$$

This equation may be used as the starting-point in deriving the inter-relationship between the dissociation energies of the As–As bond in cacodyl, and the As–I bond in dimethyliodoarsine. Representing the dissociation processes by eqns. (6*a* and *b*),

$$Me_2AsI(g) \longrightarrow Me_2As(g) + I(g) - D_1 \text{ kcal.} \quad . \; . \; . \; . \quad (6a)$$

$$Me_2As{\cdot}AsMe_2(g) \longrightarrow 2Me_2As(g) - D_2 \text{ kcal.} \quad . \; . \; . \quad (6b)$$

we obtain the appropriate thermochemical equation:

$$\Delta Hf^{\circ}(Me_2AsI, \text{g.}) - \tfrac{1}{2}\Delta Hf^{\circ}(As_2Me_4, \text{g.}) = \Delta Hf^{\circ}(I, \text{g.}) - D_1 + D_2/2 \quad . \quad (7)$$

By use of the value $\Delta Hf^\circ(\text{I, g.}) = 25{\cdot}5$ kcal. mole^{-1} (*Nat. Bur. Standards*, Circular 500), and re-writing of eqn. (5) in the form :

$$\Delta Hf^\circ(\text{Me}_2\text{AsI, g.}) - \tfrac{1}{2}\Delta Hf^\circ(\text{As}_2\text{Me}_4\text{, g.}) = \lambda_1 - \tfrac{1}{2}\lambda_2 - 9{\cdot}96 \quad . \ . \quad (8)$$

where λ_1 and λ_2 are the latent heats of evaporation of dimethyliodoarsine and cacodyl respectively, the combination of eqns. (7) and (8) then gives :

$$(D_1 - \tfrac{1}{2}D_2) = 35{\cdot}4 + \tfrac{1}{2}\lambda_2 - \lambda_1 \quad . \ . \ . \ . \ . \ . \ . \quad (9)$$

Values of λ_2 and λ_1 are not available, but by combining the vapour pressure data here reported * with other data from the literature, we calculate the values $\lambda_1 = 10{\cdot}3$ and $\lambda_2 = 9{\cdot}4$ kcal. mole^{-1}. The error in these estimates may be as much as ± 1 kcal. These values reduce eqn. (9) to :

$$(D_1 - \tfrac{1}{2}D_2) = 29{\cdot}8 \pm 1{\cdot}5 \text{ kcal. mole}^{-1} \quad . \ . \ . \ . \ . \quad (10)$$

The value of $(D_1 - \frac{1}{2}D_2)$ is appreciably larger than one would calculate from bond-energy values derived in the manner of Pauling ("Nature of the Chemical Bond," Cornell Univ. Press, New York, 1939, p. 53). Table 3 lists some mean bond energy terms ($\bar{D}$ values) of bonds to arsenic, based on thermal data taken mainly from the tables of selected values of chemical thermodynamic constants compiled by the National Bureau of Standards (Circular 500).

TABLE 3. *Mean bond energy terms of arsenic bonds.*

Molecule	ΔHf°(g.) (kcal. mole^{-1})	Bond	$\bar{D}$ (kcal.)	Molecule	ΔHf°(g.) (kcal. mole^{-1})	Bond	$\bar{D}$ (kcal.)
As	60·64	—	—	AsBr_3	− 32·0 *	As–Br	57·6
As_4	35·7	As–As	34·5	AsI_3	9·3 *	As–I	42·6
AsF_3	−218·3	As–F	111·9	As_4O_6	−283·4 *	As–O	73·3
AsCl_3	− 71·5	As–Cl	73·0	AsH_3	41	As–H	58·6

Values marked * are uncertain, owing to incomplete knowledge of the latent heats of sublimation. For AsBr_3 and AsI_3, the error in ΔHf°(g.) may be as much as ± 3 kcal. mole^{-1}, corresponding to an error of ± 1 kcal. in the derived $\bar{D}$ values.

The calculated difference (25·4 kcal.) between $\bar{D}$(As–I) and $\frac{1}{2}\bar{D}$(As–As)—from the values given in Table 3—is smaller by 4·4 kcal. than the experimental value $(D_1 - \frac{1}{2}D_2)$. The probable explanation is that the dissociation energy of the As–I bond in dimethyliodoarsine is larger than the mean As–I bond energy in arsenic tri-iodide, *i.e.*, $D_1 > \bar{D}$(As–I).

Earlier thermochemical studies on the alkylmercuric halides (Hartley, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 1019; Mortimer, Pritchard, and Skinner, *ibid.*, 1952, **48**, 220; Charnley and Skinner, *J.*, 1951, 1921) have shown that the redistribution reactions $\text{HgR}_2 + \text{HgX}_2 \longrightarrow 2\text{RHgX}$ are exothermic, from which it follows that the heat content of RHgX is larger than that calculated from the sum of the mean bond energy terms, $\bar{D}$(Hg–R) and $\bar{D}$(Hg–X), when these are derived individually from the compounds HgR_2 and HgX_2. The present results suggest that a similar exaltation in mean bond energy terms is present in the dimethylarsenic halides.

Whilst the analogy with the RHgX compounds provides a reasonable basis for assuming that $D_1 > \bar{D}$(As–I), it is useful to examine the equation we have derived, *i.e.* :

$$(D_1 - \tfrac{1}{2}D_2) = \bar{D}(\text{As–I}) - \tfrac{1}{2}\bar{D}(\text{As–As}) + 4{\cdot}4 \text{ kcal.} \quad . \ . \ . \quad (11)$$

according to the possibilities that D_2 is greater than, equal to, or less than $\bar{D}$(As–As). If $D_2 \geqslant \bar{D}$(As–As), then eqn. (11) requires that $D_1 > \bar{D}$(As–I), and that D_1 is at least 47 kcal. mole^{-1}. If the third possibility, $D_2 < \bar{D}$(As–As), were true, D_1 would remain greater than $\bar{D}$(As–I) unless D_2 were reduced by at least 8·8 kcal. relative to $\bar{D}$(As–As). Now in the As_4 molecule, the bond angles of 60° are generally considered to involve a considerable degree of strain, resulting in a weakening of the As–As bonds relative to the unstrained condition. In cacodyl, although its molecular configuration has not been

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* An attempt to measure the vapour pressure of dimethyliodoarsine over a range of temperature in an apparatus similar to that described by Burg and Schlesinger (*J. Amer. Chem. Soc.*, 1937, **59**, 674) was not successful, owing to a slow but persistent attack on mercury.

determined, there is no necessity to assume strain, and from this viewpoint one might reasonably expect that here the As–As bond is stronger than in As_4. Pauling and Simonetta (*J. Chem. Phys.*, 1952, **20**, 801) have recently discussed the analogous P_4 molecule, in which they conclude there is a total strain energy of 22·8 kcal., or 3·8 kcal. per P–P bond. A similar strain energy in As_4 would raise the $\bar{D}$ value for a normal unstrained As–As bond from 34·5 kcal. in As_4 itself to 38·3 kcal. If we identify D_2 with the latter value, the value for D_1 becomes 49·0 kcal.

The general conclusion from these considerations is that the dissociation energy of the As–I bond in dimethyliodoarsine probably lies in the range 47—50 kcal. mole^{-1}, but a more exact assessment will be possible when information on the As–As bond dissociation energy in cacodyl becomes available. The direct determination of D_2 would be of value, not only in connection with the present work, but also as an indication of the strain energy in the As_4 molecule. The suggestion by Mashima (*ibid.*, p. 801) that the bonding in P_4 and As_4 involves *spd* trigonal pyramid bond orbitals contrasts with Pauling and Simonetta's views (*loc. cit.*), and a choice between these two viewpoints should be possible from a knowledge of D_2.

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