

376. Heats of Formation and Bond Energies. Part XI.* Triphenylarsine.

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The heat of combustion of triphenylarsine in oxygen has been measured by use of a rotating-bomb calorimeter. The heat of formation is derived: $\Delta H_f^\circ(\text{Ph}_3\text{As, cryst.}) = +71.0 \pm 2.0$ kcal./mole. The mean bond-dissociation energy, $\bar{D}(\text{As-Ph}) = 60.3 \pm 4$ kcal./mole, is calculated.

HEATS of combustion of organoarsenic compounds have been measured hitherto only in static-bomb calorimeters.¹⁻³ The combustion products contain a mixture of solid arsenic oxides, elementary arsenic, carbon, unburnt compounds, and an aqueous solution of both tervalent and quinquevalent arsenic, at varying concentrations in different parts of the bomb. The mixture is difficult to analyse and is thermochemically ill-defined. By use of a rotating-bomb calorimeter, containing a solution of sodium hydroxide, it has been possible to measure the heat of combustion of triphenylarsine, where the only product is a homogeneous, aqueous solution containing sodium arsenite, sodium arsenate, sodium carbonate, and sodium hydroxide.

The thermochemical data which are required to calculate the heat of formation of triphenylarsine from this heat of combustion are either known, or can be derived from auxiliary combustion studies which are also reported here, except the heat of oxidation of sodium arsenite to sodium arsenate in sodium hydroxide solution. This has been obtained by measuring the heats of neutralisation of an aqueous solution of arsenious oxide and of an aqueous solution of arsenic oxide with sodium hydroxide.

EXPERIMENTAL

Compounds.—Triphenylarsine (Kodak) was recrystallised from absolute ethanol and zone-refined (Baird and Tatlock semi-micro apparatus), m. p. 62—62.5° (lit.,⁴ 58—60.5°). Arsenious oxide (AnalaR) and arsenic oxide (B.D.H.) were used.

Combustion Calorimetry.—Combustions were made in a rotating-bomb calorimeter (261 ml. capacity) designed and constructed by Dr. S. Sunner at the University of Lund, Sweden. Temperature was measured by noting the change in resistance, ΔR , of a platinum resistance thermometer, the characteristics of which have been given.⁵ Three separate series of experiments were carried out.

(a) The heat of combustion of triphenylarsine (0.92 g., *ca.* 0.003 mole) was measured in the bomb charged with water (30 ml.), sodium hydroxide (5.17 g.), and oxygen at 30 atm. pressure.

(b) The energy equivalent (E_s) of the standard initial calorimeter system, containing oxygen but neither sample nor water, was determined⁶ by combustion of benzoic acid (B.D.H. Thermochemical Standard, batch 76016), having $-\Delta U_b = 6.3191 \pm 0.0007$ kcal./g.; standard deviation, $\bar{s}B = \pm 0.011\%$ under recommended conditions. The "recommended" conditions⁶ were used, in that the bomb was charged with 0.78 ml. of water and oxygen at an initial pressure of 30 atm. The weight of benzoic acid burnt (1.1 g.) was slightly greater than the recommended quantity, and under these conditions had $-\Delta U_b = 6.3194 \pm 0.0007$ kcal./g.⁷ The energy equivalent is derived from the expression:

$$E_s = \{-\Delta U_b \times m(\text{benzoic}) + 10^{-3}[q_i + q_n - E_c(b)]\} / \Delta R(b),$$

* Part X, *J.*, 1963, 2039.

¹ Long and Sackman, *Trans. Faraday Soc.*, 1956, **52**, 1201.

² Lautsch, *Chem. Tech. (Berlin)*, 1958, **10**, 419.

³ Birr, *Z. anorg. Chem.*, 1961, **311**, 92.

⁴ Goddard, "Textbook of Inorganic Chemistry," ed. Newton Friend, Vol. XI, part 2, Griffin, London, 1930, p. 74.

⁵ Mortimer and Sellers, *J.*, 1963, 1978.

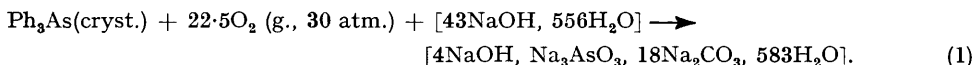
⁶ Prosen, "Experimental Thermochemistry," Vol. I, ed. Rossini, Interscience, New York, 1956, Ch. 6.

⁷ Coops, Jessup, and van Nes, "Experimental Thermochemistry," Vol. I, Ch. 3.

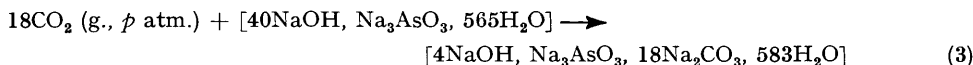
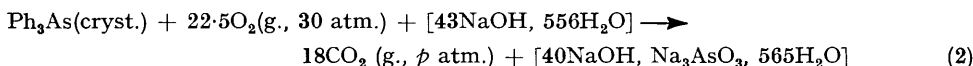
where $m(\text{benzoic})$ is the mass (*in vacuo*) of benzoic acid burnt, $E_c(b)$ is the "isothermal" correction ⁷ (in cal.) to account for the energy absorbed by the benzoic acid and water present before combustion over the temperature rise $\Delta R(b)$, q_i is the heat of combustion (3.88 kcal./g.) of cotton fuse of mass m_i , ⁷ and q_n is the heat evolved (13.81 kcal./mol) in the formation of 0.1N-nitric acid from nitrogen and water. ⁶ $E_s = 69.4673 \pm 0.0079$ kcal./ohm; standard deviation, $\bar{s}E_s = \pm 0.012\%$.

(c) A comparison ⁸ experiment was made, in which the heat of combustion of benzoic acid (0.94 g.) was determined in the bomb charged with a solution of sodium hydroxide (4.76 g.) and water (30 ml.), which corresponds to [40NaOH, 556H₂O], and with oxygen at 30 atm. pressure. The weight of benzoic acid was chosen to produce the same quantity of carbon dioxide on combustion as that produced by the weight of triphenylarsine which was burnt. The quantity of oxygen consumed by combustion of the benzoic acid, and the temperature rise, were about 15% less than for the combustion of triphenylarsine.

The overall process for the combustion of triphenylarsine, if account is taken of the oxidation of a fraction of the sodium arsenite to sodium arsenate, is represented by reaction (1), for which the change in internal energy is $\Delta U(1)$. This reaction may be considered to take place in two



stages, reactions (2) and (3), for which the changes in internal energy are $\Delta U(2)$ and $\Delta U(3)$, respectively.



The standard change in internal energy for reaction (1), $\Delta U^\circ(1)$, corresponding to the combustion of one mole of triphenylarsine, with reactants and products in their standard states, is given by:

$$\Delta U^\circ(1) = \Delta U(1) - E_c(1) + q_w(1),$$

where $E_c(1)$ is the isothermal correction due to the energy absorbed by the charge present in the bomb before combustion, over the temperature change of the reaction, and $q_w(1)$ is the thermal correction corresponding to conversion of the reactants and products into their standard states. These energy terms are expressed in units of kcal./mole of triphenylarsine burnt.

Unfortunately, there are insufficient data to calculate $E_c(1)$ and $q_w(1)$; however, it is possible to determine experimentally the approximate magnitude of the difference [$E_c(1) - q_w(1)$] from the heats of combustion of benzoic acid under recommended and comparison conditions, $\Delta U(4)$ and $\Delta U(5)$, respectively. The changes in internal energy of these reactions under standard conditions, $\Delta U^\circ(4)$ and $\Delta U^\circ(5)$, are given by:

$$\Delta U^\circ(4) = \Delta U(4) - E_c(4) + q_w(4), \text{ and } \Delta U^\circ(5) = \Delta U(5) - E_c(5) + q_w(5),$$

where $E_c(4)$ and $E_c(5)$ are the "isothermal" corrections, and $q_w(4)$ and $q_w(5)$ are the corrections to standard states for these reactions. If these energy terms are expressed in units of kcal./g. CO₂ produced, then we have:

$$\Delta U^\circ(3) = m'(\text{CO}_2)[\Delta U^\circ(5) - \Delta U^\circ(4)],$$

where $\Delta U^\circ(3)$ is the change in internal energy of reaction (3) under standard conditions; and $m'(\text{CO}_2)$ is the mass of carbon dioxide (792.18 g.) produced by the combustion of one mole of triphenylarsine. The change in internal energy, under standard conditions, for reaction (2), $\Delta U^\circ(2)$, is given by the relation:

$$\begin{aligned} \Delta U^\circ(2) &= \Delta U^\circ(1) - \Delta U^\circ(3) \\ &= [\Delta U(1) - E_c(1) + q_w(1)] - m'(\text{CO}_2)\{[\Delta U(5) - E_c(5) + q_w(5)] \\ &\quad - [\Delta U(4) - E_c(4) + q_w(4)]\}. \end{aligned}$$

* Good, Scott, and Waddington, *J. Phys. Chem.*, 1956, **60**, 1080.

Since the charges in the bomb before reactions (1) and (5) have taken place, and the temperature changes during these two reactions are almost the same, and if we take the heat capacity of benzoic acid to be the same as that of triphenylarsine, we may assume the equality,

$$E_c(1) = m'(\text{CO}_2) \cdot E_c(5),$$

with the introduction of only a very small error. The final charges, in the gaseous and liquid phases, in the bomb after reactions (1) and (5) occur are the same, and to assume the equality,

$$q_w(1) = m'(\text{CO}_2) \cdot q_w(5),$$

would also introduce only a very small thermal error. The term $\Delta U(4)$ is given by:

$$\Delta U(4) = \Delta U_b/f(\text{benzoic}) = -2.5051 \pm 0.0003 \text{ kcal./g. CO}_2,$$

where $f(\text{benzoic})$ is the mass of carbon dioxide (2.52258 g.) produced by the combustion of 1 g. of benzoic acid. Hence, the relation is derived:

$$\Delta U^\circ(2) = \Delta U(1) - m'(\text{CO}_2)[\Delta U(5) - \Delta U_b(\text{benzoic}) + E_c(4) - q_w(4)].$$

The terms $E_c(4)$ and $q_w(4)$, which refer to the combustion of benzoic acid under "recommended" conditions, can be calculated as 0.00043 and 0.00204 kcal./g. CO_2 produced, respectively. The term $\Delta U(1)$ is given by:

$$\Delta U(1) = -[M/m'(\text{Ph}_3\text{As})][E_s\Delta R(1) - 10^{-3}(q_i + q_{\text{sn}} + q_{\text{oxid}})],$$

where $m'(\text{Ph}_3\text{As})$ is the mass of triphenylarsine burnt, calculated from the relation,

$$m'(\text{Ph}_3\text{As}) = m(\text{Ph}_3\text{As})[m(\text{As}^{\text{III}}) + m(\text{As}^{\text{V}})]/[m(\text{As calc.})],$$

in which $m(\text{Ph}_3\text{As})$ is the mass of triphenylarsine in the bomb, $m(\text{As}^{\text{III}})$ and $m(\text{As}^{\text{V}})$ are the observed quantities of trivalent and quinquevalent arsenic present in the bomb after combustion as sodium arsenite and sodium arsenate, and $m(\text{As calc.})$ is that quantity of arsenic which would correspond to complete combustion of the sample; q_{sn} is the heat evolved in the formation of an aqueous solution of sodium nitrate, produced by neutralisation of nitric acid formed by oxidation of nitrogen present as impurity in the oxygen, -27.0 kcal./mole; q_{oxid} is the heat of oxidation of sodium arsenite in the alkaline solution, by molecular oxygen, to sodium arsenate in solution, -73.0 ± 0.2 kcal./mole. It was difficult to analyse the quantity of sodium nitrate formed, and it was assumed that the amount of nitric acid produced was the mean amount produced in the combustion of benzoic acid under "recommended" conditions. The term $\Delta U(5)$ is given by:

$$\Delta U(5) = [E_s\Delta R(5) - 10^{-3}(q_i + q_{\text{sn}})]/[m(\text{benzoic}) \cdot f(\text{benzoic})].$$

The standard heat of reaction (2), $\Delta H^\circ(2)$, can be derived from the relation,

$$\Delta H^\circ(2) = \Delta U^\circ(2) + \Delta nRT,$$

where Δn is the difference between the number of moles of gas before and after reaction (2). The results of these combustions of triphenylarsine and of benzoic acid under "recommended" and comparison conditions are shown in Tables 1, 2, and 3, respectively. The uncertainty associated with the value of $\Delta H^\circ(2)$ is given by the sum,

$$2\sqrt{\{[\bar{s}\Delta U(1)]^2 + [\bar{s}\Delta U(5)]^2 + (\bar{s}E_s)^2 + (\bar{s}B)^2\}}\%,$$

where $\bar{s}\Delta U(1)$ and $\bar{s}\Delta U(5)$ are the standard deviations (%) of the mean values of $\Delta U(1)$ and $\Delta U(5)$.

Analysis.—The amount of arsenic present as arsenite ions, $m(\text{As}^{\text{III}})$, in the liquid phase after combustion was determined volumetrically by titration with aqueous iodine solution. The total arsenic, $m(\text{As obs.})$, was measured gravimetrically by precipitation of arsenate ions with ammonium uranyl acetate and ignition to uranous uranate, U_3O_8 . The difference between these two determinations was taken to be the amount of arsenic present as arsenate ions after combustion, $m(\text{As}^{\text{V}})$.

* National Bureau of Standards, Circular 500, Washington, D.C., 1952.

TABLE 1.
 Triphenylarsine (*M*, 306.242).

| Experiment: | 1 | 2 | 3 | 4 | 5 | 6 |
|----------------------------------|----------|----------|----------|----------|----------|----------|
| $m(\text{Ph}_3\text{As})$ (g.) * | 0.913573 | 0.926319 | 0.919536 | 0.920294 | 0.919131 | 0.922855 |
| m_i (g.) | 0.005171 | 0.005340 | 0.006100 | 0.005183 | 0.005424 | 0.005430 |
| $\Delta R(1)$ (ohm.) | 0.12300 | 0.12389 | 0.12297 | 0.12287 | 0.12278 | 0.12324 |
| $m(\text{As}^{\text{III}})$ (g.) | 0.0944 | 0.1635 | 0.1533 | 0.1695 | 0.1586 | 0.1711 |
| $m(\text{As}^{\text{V}})$ (g.) | 0.1291 | 0.0631 | 0.0715 | 0.0556 | 0.0661 | 0.0546 |
| $m(\text{As obs.})$ (g.) | 0.223504 | 0.226667 | 0.224895 | 0.225061 | 0.224694 | 0.225704 |
| $m(\text{As calc.})$ (g.) | 0.223504 | 0.226622 | 0.224963 | 0.225150 | 0.224865 | 0.225776 |
| q_i (cal.) | 20.07 | 20.72 | 23.67 | 20.11 | 21.05 | 21.07 |
| q_{sm} (cal.) | 0.78 | 0.78 | 0.78 | 0.78 | 0.78 | 0.78 |
| q_{oxid} (cal.) | 125.8 | 61.5 | 69.7 | 54.2 | 64.4 | 53.2 |
| $-\Delta U(1)$ (kcal./mole) ... | 2815.0 | 2817.9 | 2814.4 | 2816.4 | 2815.3 | 2816.9 |

Mean $-\Delta U(1) = 2816.0$ kcal./mole (standard deviation of mean ± 0.5 kcal./mole); $\delta\Delta U(1) = \pm 0.020\%$; $\Delta U^\circ(2) = -2358.8$ kcal./mole; $\Delta nRT = -2.67$ kcal./mole; $\Delta H^\circ(2) = -2361.5 \pm 1.5$ kcal./mole.

* All weights *in vacuo*: d_{25} , 1.306 g./ml.

 TABLE 2.
 Benzoic acid (*M*, 122.125); recommended conditions.

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|----------------------------|----------|----------|----------|----------|----------|
| $m(\text{benzoic})$ (g.) * | 1.119175 | 1.123516 | 1.112167 | 1.102446 | 1.110803 |
| m_i (g.) | 0.005179 | 0.005639 | 0.004753 | 0.005290 | 0.005712 |
| ΔR_b (ohm) | 0.10211 | 0.10251 | 0.10139 | 0.10056 | 0.10138 |
| q_i (cal.) | 20.10 | 21.88 | 18.44 | 20.53 | 22.16 |
| q_n (cal.) | 0 | 0.20 | 0.20 | 0.40 | 0.40 |
| $E_s(b)$ (cal.) | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 |
| E_s (kcal./ohm) | 69.4497 | 69.4657 | 69.4918 | 69.4771 | 69.4522 |

Mean $E_s = 69.4673$ kcal./ohm (standard deviation of mean ± 0.0079 kcal./ohm); $\delta E_s = \pm 0.012\%$.

* d_{25} , 1.320 g./ml.

 TABLE 3.
 Benzoic acid (*M*, 122.125); comparison conditions.

| Experiment: | 1 | 2 | 3 | 4 | 5 |
|--|----------|----------|----------|----------|----------|
| $m(\text{benzoic})$ (g.) | 0.944610 | 0.945005 | 0.946066 | 0.943860 | 0.945842 |
| m_i (g.) | 0.005490 | 0.005618 | 0.006199 | 0.004910 | 0.006045 |
| $\Delta R(5)$ (ohm) | 0.10600 | 0.10604 | 0.10627 | 0.10580 | 0.10614 |
| q_i (cal.) | 21.31 | 21.80 | 24.06 | 19.06 | 23.46 |
| q_{sm} (cal.) | 0.78 | 0.78 | 0.78 | 0.78 | 0.78 |
| $-\Delta U(5)$ (kcal./g. CO_2 produced) | 3.0809 | 3.0806 | 3.0829 | 3.0785 | 3.0801 |

Mean $\Delta U(5) = -3.0806$ kcal./g. CO_2 (standard deviation of mean ± 0.0007 kcal./g. CO_2); $\delta\Delta U(5) = \pm 0.020\%$.

Units.—Heat terms are given in units of the thermochemical calorie, 1 cal. = 4.1840 abs. J. Weights used were calibrated against N.P.L. standards. The atomic weights used are those recommended by the International Unions in 1961,¹⁰ and all heats of formation quoted from other sources have been recalculated in terms of these atomic weights. All heat terms refer to 25°.

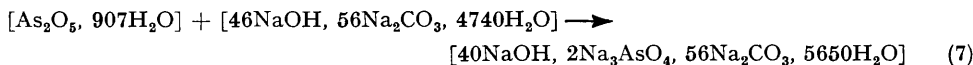
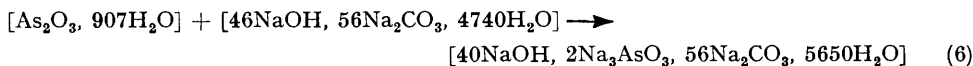
Reaction Calorimetry.—The heats of neutralisation were measured in a calorimeter which has been described in detail elsewhere.¹¹ It consisted of a cylindrical Dewar vessel (capacity 250 ml.) encased in a brass can which was immersed in a thermostat bath at 25°. A platinum resistance thermometer was used to measure temperature changes. The energy equivalent of the calorimeter and charge was determined electrically by the substitution method.

Phials of aqueous solutions (~40 ml.) of arsenious oxide and of arsenic oxide were broken

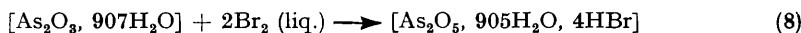
¹⁰ *J.*, 1961, 5564.

¹¹ Pedley, Skinner, and Chernick, *Trans. Faraday Soc.*, 1957, 53, 1612.

into aqueous sodium hydroxide solution (~210 ml.) in the calorimeter. The reactions are represented by equations (6) and (7). The heats of these reactions were determined as



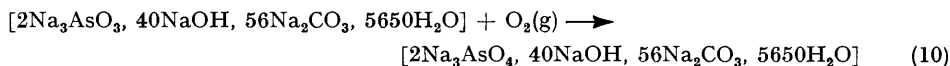
$\Delta H(6) = -9.77 \pm 0.05$, and $\Delta H(7) = -78.24 \pm 0.30$ kcal./mole. Bjellerup, Sunner, and Wadsö¹² measured the heat of the oxidation reaction (8). The arsenious oxide would be



present as the virtually undissociated acid H_3AsO_3 , whilst the arsenic oxide would be present as the acid H_3AsO_4 , partly dissociated to the ions H^+ and H_2AsO_4^- . Correcting for the heat of this ionisation, and for the heat of dilution of HBr to infinite dilution, the heat of reaction is calculated¹³ as $\Delta H(8) = -56.60 \pm 0.10$ kcal./mole. Using the heats of formation: $\text{H}_2\text{O}(\text{liq.}) = -68.3149 \pm 0.0096$,¹⁴ and $[\text{HBr}, \infty \text{H}_2\text{O}] = -29.15 \pm 0.02$ kcal./mole,¹⁵ the heat of the reaction,



in which the arsenious and arsenic oxides are in solution as undissociated acids, is calculated as -76.6 ± 0.2 kcal./mole. The heat of ionisation of the first hydrogen atom of arsenic acid is -1.69 ± 0.04 kcal./mole,¹³ and under the conditions of reaction (9) it will be about 60% ionised. Allowing for this ionisation, the heat is calculated, $\Delta H(9) = -77.6 \pm 0.2$ kcal./mole. Hence, the heat of the oxidation reaction (10) is calculated as $\Delta H(10) = -146.0 \pm 0.5$



kcal./mole. The concentrations of sodium arsenite and sodium arsenate are only one fifth of those in equation (1), and the concentration of sodium carbonate only about one third. However, since the solutions of sodium arsenite and arsenate are dilute, and the ratio of sodium hydroxide to water is the same as that in equation (1), it is reasonable to assume that $\Delta H(10)$ applies to the oxidation under the conditions of equation (1), without appreciable error being introduced.

DISCUSSION

The heat of formation of triphenylarsine can be calculated from the thermochemical equation:

$$\Delta H_f^\circ(\text{PhAs}_3, \text{cryst.}) = 18\Delta H_f^\circ(\text{CO}_2, \text{g}) + 9\Delta H_f^\circ(\text{H}_2\text{O}, \text{liq.}) + \Delta H_f^\circ[\text{Na}_3\text{AsO}_3, \text{in } 40\text{NaOH}, 565\text{H}_2\text{O}] - 3\Delta H_f^\circ[\text{NaOH}, \text{in } 12.93\text{H}_2\text{O}] - \Delta H^\circ(2) + \Delta H_d,$$

where $\Delta H_d = -0.4$ kcal./mole⁹ is the heat of dilution of sodium hydroxide solution $40[\text{NaOH}, \text{in } 12.93\text{H}_2\text{O}] \longrightarrow 40[\text{NaOH}, \text{in } 14.12\text{H}_2\text{O}]$. Schulman and Schumb¹⁶ measured

¹² Bjellerup, Sunner, and Wadsö, *Acta Chem. Scand.*, 1957, **11**, 1761.

¹³ Sellers, Sunner, and Wadsö, contribution II: 14, Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July 1963.

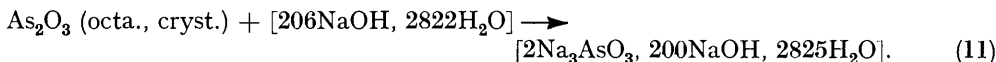
¹⁴ Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

¹⁵ Johnson and Ambrose, *J. Res. Nat. Bur. Stand.*, 1963, **67A** (*Phys. and Chem.*), 427; Sunner and Thorén, contribution II: appendix, Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July 1963.

¹⁶ Schulman and Schumb, *J. Amer. Chem. Soc.*, 1943, **65**, 879.

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the heat of solution of arsenious oxide in $\sim 4N$ -sodium hydroxide solution as $\Delta H(11) = -13.43 \pm 0.06$ kcal./mole, which refers to the reactions:



The heat of formation, $\Delta H_f^\circ[\text{Na}_3\text{AsO}_3, \text{ in } 100\text{NaOH}, 1412\text{H}_2\text{O}] = -318.93 \pm 0.28$ kcal./mole, can be calculated from the relation,

$$\Delta H_f^\circ[2\text{Na}_3\text{AsO}_3; \text{ in } 200\text{NaOH}, 2825\text{H}_2\text{O}] = \Delta H_f^\circ(\text{As}_2\text{O}_3, \text{ octa., cryst.}) - 3\Delta H_f^\circ(\text{H}_2\text{O}, \text{ liq.}) + 6\Delta H_f^\circ[\text{NaOH}, \text{ in } 13.70\text{H}_2\text{O}] + \Delta H(11) - \Delta H_d,$$

where $\Delta H_d = -0.78$ kcal./mole is the heat of dilution of sodium hydroxide solution $200[\text{NaOH}, \text{ in } 13.70\text{H}_2\text{O}] \longrightarrow 200[\text{NaOH}, \text{ in } 14.12\text{H}_2\text{O}]$, and the heats for formation are: As_2O_3 (octa., cryst.), -156.99 ± 0.3 ; ⁹ $\text{H}_2\text{O}(\text{liq.})$, -68.3149 ± 0.0096 ; ¹⁴ $[\text{NaOH}, \text{ in } 13.70\text{H}_2\text{O}]$, -112.193 ± 0.01 kcal./mole.⁹ Although the concentration of sodium arsenite in reaction (11), *i.e.*, $[0.4\text{Na}_3\text{AsO}_3, 40\text{NaOH}, 565\text{H}_2\text{O}]$, is lower than that produced in reaction (2), *i.e.*, $[\text{Na}_3\text{AsO}_3, 40\text{NaOH}, 565\text{H}_2\text{O}]$, the ratio of sodium hydroxide to water is the same, and as the heat of dilution of sodium arsenite at these low concentrations is likely to be very small, the heat of formation is taken to be the same in both cases. Incorporating the additional heats of formation: $\text{CO}_2(\text{g})$, -94.0517 ± 0.0108 ; ¹⁴ and $[\text{NaOH}, \text{ in } 12.93\text{H}_2\text{O}]$, -112.187 ± 0.01 kcal./mole, the value is derived, $\Delta H_f^\circ(\text{Ph}_3\text{As}, \text{ cryst.}) = +71.0 \pm 2.0$ kcal./mole. This may be compared with a value of $+81.2 \pm 2.0$ kcal./mole, obtained by Birr³ from measurement of the heat of combustion of triphenylarsine, using a static-bomb calorimeter.

The latent heat of sublimation of triphenylarsine has not been measured, but since the melting and boiling points of this compound are close to those of triphenylphosphine, for which a latent heat of sublimation of 21.0 ± 0.5 kcal./mole has been estimated,¹⁷ it is likely that the value for triphenylarsine will be very similar. Using this value, the heat of formation is derived, $\Delta H_f^\circ(\text{Ph}_3\text{As}, \text{g}) = +92.0 \pm 2.5$ kcal./mole. The mean bond-dissociation energy, $\bar{D}(\text{As-Ph})$, for the arsenic-carbon bonds can be calculated from the relation:

$$\bar{D}(\text{As-Ph}) = \Delta H_f^\circ(\text{Ph}, \text{g}) + (1/3)\Delta H_f^\circ(\text{As}, \text{g}) - (1/3)\Delta H_f^\circ(\text{Ph}_3\text{As}, \text{g}).$$

Taking our value for the heat of formation of gaseous triphenylarsine and the heats of formation, $\text{Ph}(\text{g})$, $+71 \pm 3$ kcal./mole,¹⁸ and $\text{As}(\text{g})$, 60.0 kcal./g.-atom.¹⁹ we obtain the mean bond-dissociation energy $\bar{D}(\text{As-Ph}) = 60.3 \pm$ kcal./mole.

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¹⁷ Bedford, Heinekey, Millar, and Mortimer, *J.*, 1962, 2932.

¹⁸ Mortimer, "Reaction Heats and Bond Strengths," Pergamon, Oxford, 1962, p. 129.

¹⁹ Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 2nd edn., 1958.