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ENTHALPY OF COMBUSTION OF TRIPHENYLARSINE OXIDE

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ABSTRACT

The standard enthalpy of combustion of triphenylarsine oxide has been measured by use of a rotating-bomb combustion calorimeter. The enthalpy of formation, $\Delta H_f^\ominus(\mathrm{Ph_3AsO, c}) = 18.8 \pm 3.5$ kcal $\mathrm{mol^{-1}}$ has been calculated, from which the bond dissociation energy $D(\mathrm{Ph_3As{=}O}) = 102.6 \pm 7.3$ kcal $\mathrm{mol^{-1}}$ has been obtained.

In a previous paper [1] we have reported determination of the enthalpy of combustion, in the presence of a sodium hydroxide solution, of triphenylarsine, by use of a rotating-bomb combustion calorimeter. It was then possible to calculate the enthalpy of formation of triphenylarsine in terms of the enthalpy of formation of an aqueous solution of sodium arsenite, which is the product of combustion. The purpose of the work reported in this paper was to establish whether this method is applicable to the determination of the enthalpy of formation of an organoarsenic compound containing pentavalent arsenic. Measurement of the enthalpy of combustion of triphenylarsine oxide, $\mathrm{Ph_3AsO}$, is described.

Triphenylarsine oxide (Koch-Light Ltd.) was purified by zone-refinement (Baird and Tatlock semi-micro apparatus), m.p. 469 K. Sodium arsenite and sodium hydroxide (B.D.H.) were dissolved in de-ionised, distilled water.

Combustions were made in a rotating-bomb calorimeter (261 $\mathrm{cm^3}$ capacity) designed by Professor S. Sunner and constructed at the University of Lund, Sweden. Temperature was measured by noting the change in resistance, ΔR, of a platinum resistance thermometer. Two series of experiments were carried out.

(a) The energy of combustion of triphenylarsine oxide (ca. 0.9 g, 0.003 mol), contained in a fused silica crucible, was measured in the bomb charged

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with water (50 cm^3) sodium hydroxide (6 12 g) and oxygen (30 atm pressure *) The amount of arsenic present as arsenite ions $m(As^{III})$ in the liquid phase after combustion was determined volumetrically by titration with 0 02 N potassium bromate solution The arsenic present as arsenate ions, $m(As^{V})$, was assumed to be the difference between the mass of arsenic in the triphenylarsine oxide present initially and $m(As^{III})$ Between 75 and 76 mol% of the total arsenic appeared as arsenite ions

(b) A comparison experiment was made in which benzoic acid (ca 0 88 g), in a fused silica crucible, was burned in a bomb charged with water (50 cm^3), oxygen (30 atm pressure), and quantities of sodium arsenite and sodium hydroxide such that their concentrations, after combustion, would be the same as those present after the combustions in the series (a) experiments

We have adopted the same procedure as that reported for the combustion of triphenylarsine [1]. In the series (b) experiments, the mass of benzoic acid was chosen so as to produce the same mass of CO_2 as that produced by combustion of triphenylarsine oxide in the series (a) experiments The temperature rise on combustion of this amount of benzoic acid was about 10% less than that for the triphenylarsine combustions Data from the series (b) experiments have been used to calculate an apparent energy of solution of gaseous carbon dioxide, Δu, which is then used to derive the correction, q_{CO_2}, in the calculation of $\Delta U^{\ominus}$ for the combustion reaction (1) (below)

The energy equivalent, ε_{sf}, of the standard calorimeter had been determined previously [2] as 68648 ± 8 cal ohm^{-1} All combustions were initiated electrically at 298 15 K and the bomb was rotated after combustion in every experiment Weights used were calibrated against NPL standards The atomic weights used are those recommended by the IUPAC Commission [3] Uncertainty intervals are given as twice the standard deviation of the mean values

The results of the two series of experiments are shown in Tables 1 and 2, where the symbols have the following meanings $m(Ph_3AsO)$, m_t, and $m(B\,A)$ are the masses of triphenylarsine oxide, cotton, and benzoic acid, respectively $m(As^{III})$ and $m(As^{V})$ are the masses of trivalent and pentavalent arsenic present after combustion ΔR_a and ΔR_b are the corrected changes in resistance of the platinum resistance thermometer for experiments (a) and (b), respectively

q_t is the heat evolved (3881 cal g^{-1}) by the combustion of the cotton fuse [1] q_{sn} is the heat evolved (27 0 kcal mol^{-1}) by the formation of sodium nitrate from nitrogen, water and sodium hydroxide solution [1] q_{oxid} is the heat evolved ($68\ 8 \pm 0\ 1$ kcal mol^{-1}) on the oxidation, by molecular oxygen, of an aqueous solution of sodium arsenite to sodium arsenate, under the conditions in the bomb after combustion [4] $q_{B\,A}$ is the heat evolved from a

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* Throughout this paper atm = 760 torr = 101 325 kPa, 1 cal = 4 184 J

TABLE I

Experiment (a) combustion of triphenylarsine oxide, $m(\mathrm{Ph_3AsO}) = 322\ 239$

Experiment	1	2	3	4	5
$m(\mathrm{Ph_3AsO})$ (g)	0 89647(5)	0 88322(0)	0 88594(0)	0 88366(0)	0 88338(0)
m_1 (g)	0 00610(0)	0 00645(0)	0 00558(0)	0 00612(5)	0 00604(0)
ΔR_a (ohm)	0 11174	0 11013	0 11067	0 11027	0 11005
$m(\mathrm{As^V})$ (g)	0 05197	0 04980	0 04787	0 04952	0 04908
$m(\mathrm{As^{III}})$ (g)	0 15646	0 15555	0 15811	0 15593	0 15631
g_1 (cal)	23 67	25 03	21 66	23 77	23 44
q_{sn} (cal)	0 00	0 00	0 00	0 00	0 00
q_{oxid} (cal)	47 72	45 73	43 96	45 47	45 07
$q_{\mathrm{CO_2}}$ (cal)	1248 36	1230 39	1233 37	1230 71	1230 24
ε_a (cal ohm^{-1})	541	541	541	541	541
$-\Delta U^{\ominus}(1)$ (kcal mol^{-1})	2304 6	2305 3	2312 6	2308 2	2303 8

Mean $\Delta U^{\ominus}(1) = -2306\ 9 \pm 3\ 2$ kcal mol^{-1}

$\Delta nRT = -2\ 4$ kcal mol^{-1}

$\Delta H^{\ominus}(1) = -2309\ 3 \pm 3\ 2$ kcal mol^{-1}

TABLE 2

Comparison experiment (b)

Experiment	1	2	3	4	5	6
m(B A) (g)	0 87978(0)	0 88264(5)	0 88532(5)	0 88408(5)	0 88674(0)	0 88500(0)
m_i (g)	0 00588(5)	0 00560(0)	0 00550(0)	0 00614(0)	0 00614(5)	0 00577(0)
ΔR_b (ohm)	0 09889	0 09908	0 09936	0 09923	0 09968	0 09940
$q_{B A}$ (cal)	5554 56	5572 65	5589 57	5581 74	5598 50	5587 52
q_i (cal)	22 84	21 73	21 35	23 83	23 85	22 39
q_{sn} (cal)	2 70	2 70	2 70	2 70	2 70	2 70
ε_b (cal ohm^{-1})	545	545	545	545	545	545
$-\Delta w$ (cal per g CO_2)	566 36	562 93	562 54	561 44	566 15	564 32
Mean $\Delta w = -563\ 96 \pm 1\ 6$ cal per g CO_2						

quantity of benzoic acid, equal to the product of its mass and its standard energy of combustion, $\Delta U^{\ominus} = -6313.58$ cal g^{-1}. q_{CO_2} is the apparent heat evolved by solution of carbon dioxide in the bomb solution, given by

$$q_{CO_2} = \left[m(CO_2) \times m(\text{B.A.}) + m'(CO_2) \times m_{\text{i}}\right] \Delta u$$

where $m(CO_2)$ and $m'(CO_2)$ are the masses of carbon dioxide produced by 1 g of benzoic acid (2.5227 g) and 1 g of cotton fuse (1.618 g), respectively, and where Δu is given by the expression

$$-\Delta u = \frac{(\varepsilon_{sf} + \varepsilon_b)\,\Delta R_b - (q_{\text{B.A.}} + q_{\text{i}} + q_{sn})}{m(CO_2) \times m(\text{B.A.}) + m'(CO_2) \times m_{\text{i}}} \text{cal per g } CO_2$$

where ε_{sf} is the energy equivalent of the standard calorimeter after combustion, which excludes the contribution made by crucible, solution and oxygen, and where ε_b is the energy equivalent of the crucible, solution and oxygen present after combustion in the series (b) experiments.

The value for the standard enthalpy of reaction (1) $\Delta H^{\ominus}(1)$ is calculated from the relationship $\Delta H^{\ominus}(1) = \Delta U^{\ominus}(1) + \Delta nRT$, where

$$\Delta U^{\ominus}(1) = 10^{-3}\Big[(\varepsilon_{sf} + \varepsilon_a)R_a - (q_{\text{i}} + q_{sn} + q_{\text{oxid}} + q_{CO_2}) \\ \times [M(Ph_3AsO)]/m(Ph_3AsO)\Big] \text{kcal mol}^{-1}$$

where ε_a is the energy equivalent of the crucible, solution and oxygen present after combustion, in the series (a) experiments and $M(Ph_3AsO)$ is the molecular weight of triphenylarsine oxide. The value $\Delta H^{\ominus}(1) = -(2309.3 \pm 3.2)$ kcal mol^{-1} is obtained.

$$C_{18}H_{15}AsO(cr) + 22O_2(g) + 56[NaOH, 18H_2O](sln) \\ \rightarrow 18CO_2(g) + [NaAsO_2, 55NaOH, 1016H_2O](sln) \qquad (1)$$

$$\tfrac{1}{2}As_2O_3(\text{octa, cr}) + 56[NaOH, 18.13H_2O](sln) \\ \rightarrow [NaAsO_2, 55NaOH, 1016H_2O](sln) \qquad (2)$$

$$56[NaOH, 18.13H_2O](sln) - 7.5H_2O(l) \rightarrow 56[NaOH, 18H_2O](sln) \qquad (3)$$

$$C_{18}H_{15}AsO(cr) + 22O_2(g) \rightarrow 18CO_2(g) + 7.5H_2O(l) + \tfrac{1}{2}As_2O_3(\text{octa, cr}) \qquad (4)$$

The value $\Delta H(4) = -2302.7 \pm 3.2$ kcal mol^{-1} is then derived from the relationship $\Delta H(4) = \Delta H(1) - \Delta H(2) + \Delta H(3)$. The value $\Delta H(2) = \tfrac{1}{2}(-13.15 \pm 0.06$ kcal per mol $As_2O_3) = -6.58 \pm 0.03$ kcal is found from an interpolation of the measured enthalpies of solution of As_2O_3(octa, cr) in $[NaOH, 13.7H_2O](sln)$ -13.43 ± 0.06 kcal mol^{-1} [5], in $[NaOH, 29H_2O](sln)$ -12.03 ± 0.04 kcal mol^{-1} [6], and in $[NaOH, 52H_2O](sln)$ -10.53 ± 0.07 kcal mol^{-1} [7]. The value $\Delta H(3) = -0.01$ kcal mol^{-1} is obtained by interpolation of literature data [8].

Using the $\Delta H_f^\ominus$ values $CO_2(g)$ $-94\ 051$ kcal mol^{-1}, $H_2O(l)$ -68.315 kcal mol^{-1} [9] and As_2O_3(octa , cr) $-157\ 1 \pm 0\ 3$ kcal mol^{-1}, we calculate the value $\Delta H_f^\ominus(Ph_3AsO, cr) = +18.8 \pm 3\ 5$ kcal mol^{-1} A Knudsen effusion technique [10] has been used to obtain the enthalpy of sublimation of Ph_3AsO as $\Delta H_{sub}^{410} = 34\ 2 \pm 1\ 3$ kcal mol^{-1} and $\Delta H_{sub}^{298} = 35\ 6 \pm 1\ 3$ kcal mol^{-1}, which leads to the value $\Delta H_f^\ominus(Ph_3AsO, g) = +54\ 4 \pm 4\ 8$ kcal mol^{-1} Combined with our previous value for $\Delta H_f^\ominus(Ph_3As, g)$ which has been updated by Pilcher and Skinner [11] to a value $+97.5 \pm 2\ 5$ kcal mol^{-1}, and $\Delta H_f^\ominus(O, g) = 59.55$ kcal mol^{-1} [9], the enthalpy of the gas phase dissociation process $Ph_3AsO(g) \rightarrow Ph_3As(g) + O(g)$, $D(As{=}O) = 102\ 6 \pm 7\ 3$ kcal mol^{-1}

We take this opportunity to correct our previously reported [6] value for the enthalpy of formation of arsenious oxide $\Delta H_f^\ominus(As_2O_3$, c, octahedral) = $-160\ 3 \pm 0\ 2$ kcal mol^{-1} This had been determined from measurements of the enthalpy of formation of $AsBr_3$, and the enthalpies of solution of $AsBr_3$ and As_2O_3 in aqueous sodium hydroxide An ancillary measurement was of the enthalpy of solution of sodium bromide (equation 8 of ref 6), $3NaBr(c) + [NaAsO_2, 64NaOH, 2000H_2O](l) \rightarrow [NaAsO_2, 3NaBr, 64NaOH, 2000H_2O]$ for which we quoted a value $\Delta H = -0\ 63$ kcal per 3 mol NaBr

Minor et al [7] obtained a value $\Delta H_f^\ominus(As_2O_3$, c, octahedral) = $-157\ 4 \pm 0\ 5$ kcal mol^{-1}, by use of a similar approach, using $AsCl_3$ in place of $AsBr_3$ This led them to check our enthalpy of solution measurements, and suggest [12] that the discrepancy between the two values for the enthalpy of formation of As_2O_3 probably lay in an arithmetic error on our part, and that our quoted value for the enthalpy of solution of NaBr, $\Delta H = -0\ 63$ kcal, should refer to one mole of NaBr

We have remeasured the enthalpy of this reaction (equation 8 of ref 6), using the LKB 8700 calorimeter, and have obtained a value $\Delta H = -0\ 80 \pm 0\ 01$ kcal per mol NaBr. Using this value and our previous data [6] leads to $\Delta H_f^\ominus(As_2O_3$, c, octahedral) = $-156\ 8 \pm 0\ 2$ kcal mol^{-1}, which is the same as that obtained by Minor et al [7], within the combined error limits The mean value of $-157\ 1 \pm 0.3$ kcal mol^{-1}, which we have used in the calculation of $\Delta H_f^\ominus(Ph_3AsO, cr)$, is virtually the same as that presently quoted ($-157\ 02$ kcal mol^{-1}) in the National Bureau of Standards Note 270-3 [13]

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