236. *The Thermochemistry of Organo-arsenic Compounds. Part II.* Esters of Arsenious Acid.*

By T. CHARNLEY, C. T. MORTIMER, and H. A. SKINNER.

Values are reported for the heats of hydrolysis in 4N-sodium hydroxide at 25° of trimethyl, triethyl, and tripropyl arsenite. The heats of formation of the esters have been derived as follows (in kcal./mole):

ΔH_f° [As(OMe)$_3$, liq.] $= -141{\cdot}3 \pm 0{\cdot}7$; ΔH_f°[As(OEt)$_3$, liq.] $= -168{\cdot}8 \pm 0{\cdot}7$; ΔH_f° [As(OPr)$_3$, liq.] $= -190{\cdot}0 \pm 1{\cdot}6$.

From measurements of the vapour pressures over a range of temperature, latent heats of vaporization were obtained:

$\Delta H_{\text{vap.}}(\text{Me}_3\text{AsO}_3) = 10{\cdot}06 \pm 0{\cdot}14$, $\Delta H_{\text{vap.}}(\text{Et}_3\text{AsO}_3) = 11{\cdot}76 \pm 0{\cdot}46$ kcal./mole.

The thermal data are used to derive values of the *mean* bond dissociation energies, $\bar{D}$(As–OR), in the alkyl arsenites. The variations in these $\bar{D}$ values are discussed.

THE lower members of the series of esters of arsenious acid, As(OR)$_3$, are rapidly and completely hydrolysed by water to give the alcohols, ROH, and precipitated arsenious oxide. For the purpose of thermochemical study, hydrolysis in the presence of excess of alkali, yielding products *in solution*, is preferable to aqueous hydrolysis, and was the method adopted in the present work.

The heats of hydrolysis provide values for the heats of formation of the esters, ΔH_f°[As(OR)$_3$], in terms of the heat of formation of arsenious oxide. The latter is reasonably well established, and we have accepted the value, ΔH_f°(As$_2$O$_3$, cryst., octahedral) $= -156{\cdot}97$ kcal./mole, recommended in the "Tables of Selected Values of Chemical Thermodynamic Properties" (Nat. Bur. Standards, Washington, Circular 500, 1952).

The thermochemical results can be translated into values for the *mean* bond dissociation energies, $\bar{D}$(As–OR), in this series of esters, by use of a procedure similar to that of Charnley, Skinner, and Smith (*J.*, 1952, 2288) in a comparable study on the esters of boric acid.

EXPERIMENTAL

Preparation of Compounds.—The arsenious esters were prepared by Crafts's method (*Bull. Soc. chim.*, 1870, **14**, 102), *viz.*, reaction of the appropriate sodium alkoxide with excess of arsenic trichloride. Unchanged arsenic trichloride was removed by precipitation with gaseous ammonia. The crude esters were purified by fractional distillation under reduced pressure through a 6" column packed with stainless steel gauze, designed by Imperial Chemical Industries Limited, Billingham. Samples were retained boiling over the ranges given below: As(OMe)$_3$ 27·2—27·4°/10 mm.; As(OEt)$_3$ 46·3—46·6°/6 mm.; As(OPr)$_3$ 81·3—81·6°/5·5 mm. These were further distilled in a high vacuum, and the pure products collected and sealed in thin, weighed, glass ampoules.

Calorimeter.—The calorimeter was identical with that described in Part I (*loc. cit.*). The experiments were conducted by breaking the ampoules containing known amounts of ester under the surface of 750 c.c. of 4N-sodium hydroxide in the Dewar vessel. As a precaution against atmospheric oxidation of the products, a slow stream of moist nitrogen was passed over the surface of the solution throughout the experiments. Temperature changes were measured in terms of the resistance changes 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, defined as: 1 calorie = 4·1840 abs. joules. The reactions were performed at 25°.

Results.—Preliminary experiments, in which ampoules of trimethyl arsenite were broken under water, showed that the hydrolysis occurs extremely rapidly, but that subsequent dissolution of the resulting arsenious oxide is slow. This feature renders the purely aqueous hydrolysis less satisfactory for thermal study than the hydrolysis by aqueous alkali, in which arsenious oxide dissolves comparatively speedily. Schulman and Schumb (*J. Amer. Chem. Soc.*,

---

* Part I, *J.*, 1952 4331.

1943, **65**, 879) reported values for the heats of solution of the two crystalline forms of arsenious oxide in 4N-sodium hydroxide, and this fact decided our choice of medium for the hydrolysis reactions.

The observed heats of reaction in 4N-sodium hydroxide are given under ΔH_{obs} in Table 1. These values refer to the overall reactions :

$$2\text{As(OR)}_3\ (\text{liq.}) + 3\text{H}_2\text{O, in excess of 4N-NaOH} \longrightarrow (6\text{ROH} + \text{As}_2\text{O}_3)\text{, dissolved in 4N-NaOH} \quad (1)$$

The values given under $\Delta H_{\text{hyd.}}$ are the heats of the ideal hydrolysis reactions :

$$2\text{As(OR)}_3\ (\text{liq.}) + 3\text{H}_2\text{O}\ (\text{liq.}) \longrightarrow 6\text{ROH}\ (\text{liq.}) + \text{As}_2\text{O}_3\ (\text{octahedral}) \quad . \quad . \quad . \quad (2)$$

The relation between $\Delta H_{\text{obs.}}$ and $\Delta H_{\text{hyd.}}$ is expressed by

$$\Delta H_{\text{hyd.}} = \Delta H_{\text{obs.}} - \Delta H_{\text{soln.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta H_{\text{soln.}}$ = heat of solution of the products of reaction (2) in excess of 4N-sodium hydroxide.

The terms contributing to $\Delta H_{\text{soln.}}$ include (*a*) the heat of solution of crystalline (octahedral) arsenious oxide in 4N-sodium hydroxide, for which Schulman and Schumb (*loc. cit.*) quote $\Delta H = -13{\cdot}42 \pm 0{\cdot}1$ kcal./mole of As_2O_3, and (*b*) the heats of solution of the alcohols (ROH liq.) in 4N-sodium hydroxide. These were measured for each of the three alcohols concerned, under conditions adjusted to match those in the corresponding ester hydrolyses. The following values (in kcal./mole of ROH) were obtained : MeOH(liq.) = −1·85 ± 0·01; EtOH(liq.) = −1·58 ± 0·01; PrOH(liq.) = −1·13 ± 0·10 : these values differ appreciably from those obtained for solution in pure water (Charnley, Skinner, and Smith, *loc. cit.*).

TABLE 1. *Heats of hydrolysis of alkyl arsenites.*

R_3AsO_3 (g.)	$-\Delta H_{\text{obs.}}$ (kcal.)	$-\Delta H_{\text{hyd.}}$ (kcal.)	R_3AsO_3 (g.)	$-\Delta H_{\text{obs.}}$ (kcal.)	$-\Delta H_{\text{hyd.}}$ (kcal.)	R_3AsO_3 (g.)	$-\Delta H_{\text{obs.}}$ (kcal.)	$-\Delta H_{\text{hyd.}}$ (kcal.)
Methyl arsenite			Ethyl arsenite			Propyl arsenite		
4·6838	36·7	12·2	3·1286	35·4	12·5	5·6951	31·5	11·3
4·2266	35·7	11·2	2·5846	35·7	12·8	5·2899	31·6	11·4
4·3435	36·0	11·5	4·4918	35·5	12·6	4·7982	32·3	12·1
4·3507	35·8	11·3	3·8344	35·6	12·7	3·8306	31·7	11·5
4·0938	36·6	12·1	3·5562	35·7	12·8	6·5557	32·5	12·3
4·4704	36·1	11·6		Mean −12·7 ± 0·3			Mean −11·7 ± 1·2	
3·8930	36·3	11·8						
	Mean −11·7 ± 0·6							

The values of $\Delta H_{\text{soln.}}$ appropriate to equation (3) are thus : −24·52 ± 0·16, −22·90 ± 0·16, and −20·20 ± 0·7 kcal./mole for R = Me, Et, and Pr, respectively.

TABLE 2. *Heats of formation of alkyl arsenites,* R_3AsO_3.

R	ΔH_f° (liq.) * (kcal./mole)	ΔH_f° (gas) (kcal./mole)	R	ΔH_f° (liq.) * (kcal./mole)	ΔH_f° (gas) (kcal./mole)	R	ΔH_f° (liq.) * (kcal./mole)	ΔH_f° (gas) (kcal./mole)
Me	−141·3 ± 0·7	−131·2 ± 0·9	Et	−168·8 ± 0·7	−157·0 ± 1·2	Pr	−190·0 ± 1·6	−177·4 ± 2·1

* The errors quoted are the overall errors, obtained by *addition* of the experimental errors in our measurements, and errors present in assumed thermal data.

Table 2 gives the heats of formation of the alkyl arsenites, derived from the equation :

$$\Delta H_f^\circ\ [\text{As(OR)}_3,\ \text{liq.}] = 3\Delta H_f^\circ\ (\text{ROH, liq.}) + \tfrac{1}{2}\Delta H\ ^\circ\ (\text{As}_2\text{O}_3,\ \text{c., octa.}) - \tfrac{3}{2}\Delta H_f^\circ\ (\text{H}_2\text{O, liq.}) - \tfrac{1}{2}\Delta H_{\text{hyd.}} \quad (4)$$

which is the thermal description of the ideal hydrolysis reaction in equation (2). The values adopted for the standard heats of formation on the right-hand side of equation (4) were, in kcal./mole, as follows: MeOH(liq.) = −57·04 ± 0·05, EtOH(liq.) = −66·39 ± 0·10, PrOH(liq.) = −73·27 ± 0·25, H_2O(liq.) = −68·32 ± 0·01, and As_2O_3 (c., octa.) = −156·97 ± 0·5.

The ΔH_f° [As(OR)$_3$, gas] values, also given in Table 2, are related to the ΔH_f° obtained from equation (4) through :

$$\Delta H_f^\circ\ [\text{As(OR)}_3,\ \text{gas}] = \Delta H_f^\circ\ [\text{As(OR)}_3,\ \text{liq.}] + \Delta H_{\text{vap.}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\Delta H_{\text{vap.}}$ is the heat of vaporisation of As(OR)_3. The latent heats of vaporisation of the methyl and ethyl esters were obtained from a series of measurements over a range of temperature of the vapour pressures of the two compounds, in an apparatus similar to that described by Schlesinger and Burg (*J. Amer. Chem. Soc.*, 1937, **59**, 780). The results obtained are summarized in Table 3; values of $\Delta H_{\text{vap.}}$ were calculated from the Clausius–Clapeyron equation.

TABLE 3. *Vapour pressure,* p,* *of methyl and ethyl arsenite.*

Temp. (° C)	Me_3AsO_3, p	Et_3AsO_3, p	Temp. (° C)	Me_3AsO_3, p	Et_3AsO_3, p	Temp. (° C)	Me_3AsO_3, p	Et_3AsO_3, p
27·0°	10·7	—	42·0°	24·0	4·83	57·0°	49·5	11·12
32·0	14·0	2·46	47·0	30·9	6·48	62·0	62·1	14·59
37·0	18·5	3·47	52·0	39·2	8·53	67·0	—	18·58

* Values of p in mm. of Hg of d 13·60. The average error in the pressure readings is *ca.* 1% for $As(OMe)_3$, and 4% for $As(OEt)_3$.

The vapour pressures in Table 3 may be expressed by $\log_{10} p = -m/T + c$ (with T in °K), and where $m = 2200$, $c = 8{\cdot}358 \pm 0{\cdot}003$ for $As(OMe)_3$, and $m = 2570$, $c = 8{\cdot}831 \pm 0{\cdot}008$ for $As(OEt)_3$. The calculated values of $\Delta H_{\text{vap.}}$ are respectively $10{\cdot}06 \pm 0{\cdot}14$ and $11{\cdot}76 \pm 0{\cdot}46$ kcal./mole, respectively. The value of $\Delta H_{\text{vap.}}$ for $As(OPr)_3$ ($12{\cdot}6 \pm 0{\cdot}5$ kcal./mole) was obtained by combining our observed b. p. (at 5·5 mm.) with others from the literature, and constructing from these the pressure–temperature equation for this compound.

DISCUSSION

We define the *mean* bond dissociation energy, $\bar{D}$(As–OR), in an alkyl arsenite $As(OR)_3$, as one-third of the heat of the dissociation process :

$$\mathrm{As(OR)_3\ (g.)} \longrightarrow \mathrm{As\ (g.)} + 3\ {\cdot}\mathrm{OR\ (g.)} \qquad . \ . \ . \ . \ . \ . \ . \ (6)$$

The defining thermochemical equation is thus

$$\bar{D}(\mathrm{As{-}OR}) = \tfrac{1}{3}\Delta H_f^\circ\ (\mathrm{As,\ g.}) + \Delta H_f^\circ\ ({\cdot}\mathrm{OR,\ g.}) - \tfrac{1}{3}\Delta H_f^\circ\ [\mathrm{As(OR)_3,\ g.}] \qquad . \ . \ . \ . \ (7)$$

Of the terms in equation (7), those in ΔH_f° [$As(OR)_3$, g.] are given in Table 2, and the value ΔH_f° (As, g.) = 60·64 kcal./mole is recommended in the National Bureau of Standards tables (*loc. cit.*). The terms in ΔH_f° (·OR, g.) present some difficulty, for only in one case (·OR = ·OEt) is the value satisfactorily established. Rebbert and Laidler recently (*J. Chem. Physics*, 1952, **20**, 574) obtained ΔH_f° (·OEt, g.) = $-8{\cdot}1 \pm 1$ kcal./mole, from a study of the kinetics of thermal decomposition of diethyl peroxide.

Charnley, Skinner, and Smith (*loc. cit.*), following a suggestion by Gray (*Discuss. Faraday Soc.*, 1951, **10**, 310), derived ΔH_f° (·OEt, g.) = $-8{\cdot}7$ kcal./mole, by equating the activation energy of the unimolecular decomposition of ethyl nitrite (Steacie and Shaw, *J. Chem. Physics*, 1934, **2**, 345) to the heat of rupture of the O–N bond. This estimate is in good agreement with Rebbert and Laidler's value, and lends support to the estimate of ΔH_f° (·OMe, g.) = $-1{\cdot}9$ kcal./mole, obtained from a similar argument applied to methyl nitrite. For our present purpose, we adopt the value ΔH_f° (·OMe, g.) = $-1{\cdot}3$ kcal./mole ; this preserves the *difference* ($-6{\cdot}8$ kcal.) between the heats of formation of ·OMe and ·OEt given by Charnley *et al.*, whilst alteration is made to adjust ΔH_f° (·OEt, g.) to Rebbert and Laidler's value. Lack of suitable experimental data prevents an estimate by similar methods of ΔH_f° (·OPr, g.), and for this quantity we adopt a provisional value, ΔH_f° (·OPr, g.) = -13 kcal./mole, obtained by consideration of the probable trend in D(RO–H) in the series of aliphatic alcohols. With these values of ΔH_f° (·OR, g.), equation (7) leads to the values of $\bar{D}$(As–OR) listed in Table 4. For comparison, values of $\bar{D}$(B–OR) in the alkyl borates (Charnley, Skinner, and Smith, *loc. cit.*), and of D(H–OR) in the alcohols are also given.

TABLE 4. *Mean bond-energy values.*

·OR	ΔH_f° (·OR, g.), (kcal./mole)	$\bar{D}$(As–OR), (kcal.)	$\bar{D}$(B–OR), (kcal.)	D(H–OR) (kcal.)
·OMe	$-1{\cdot}3 \pm 2$	$62{\cdot}64 \pm 2{\cdot}3$	$103{\cdot}0 \pm 2{\cdot}3$	98·9
·OEt	$-8{\cdot}1 \pm 1$	$64{\cdot}45 \pm 1{\cdot}4$	$104{\cdot}67 \pm 1{\cdot}4$	100·3
·OPr	-13 ± 2	$66{\cdot}44 \pm 2{\cdot}7$	$106{\cdot}37 \pm 2{\cdot}8$	101·3

It is noteworthy that the D(As–OR) values are smaller than the *mean* bond dissociation of the As–O bonds in gaseous As_4O_6, for which the value D(As–O) = 73·3 kcal./mole has been derived (Part I, *loc. cit.*). One possible cause of this may lie in the resonance (" hyperconjugation ") stabilization of the radicals ·OR (cf. Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339).

To illustrate this, we may consider the values of $\bar{D}$(Me–O) and D(Me–OMe) in dimethyl ether. One may derive from existing thermal data [ΔH_f° (Me_2O, g.) = −44·3 kcal./mole (N.B.S. Tables, *loc. cit.*); ΔH_f° (Me, g.) = 32·6 ± 1 kcal./mole (Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220)]

$$(1)\ \mathrm{Me_2O\ (g.)} \longrightarrow \mathrm{2Me\ (g.)} + \mathrm{O\ (g.)};\ \Delta H_1 = 168{\cdot}6\ \text{kcal.}$$

$$(2)\ \mathrm{Me_2O\ (g.)} \longrightarrow \mathrm{Me\ (g.)} + \cdot\mathrm{OMe\ (g.)};\ \Delta H_2 = 75{\cdot}6\ \text{kcal.}$$

whence $\bar{D}$(Me–O) = $\frac{1}{2}\Delta H_1$ = 84·3 kcal., and D(Me–OMe) = ΔH_2 = 75·6 kcal. mole. The difference between these values (8·7 kcal.) is comparable with that between $\bar{D}$(As–O) and $\bar{D}$(As–OMe), and arises, we suggest, from resonance stabilization in the methoxy-radical. There is reason to believe that there is an appreciable resonance stabilization in the *ethyl* radical, arising from π-hyperconjugation (cf. Wheland, *J. Chem. Physics*, 1934, **2**, 474; Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41), and one might expect a similar effect in the *methoxy*-radical, particularly if the oxygen atom adopts a trigonal, or near-trigonal disposition of its bonded electron pair with respect to its two lone-pairs of non-bonding electrons, leaving the odd electron free to conjugate, as a π-electron, with the $-\mathrm{C{\equiv}H_3}$ group.

The variations in $\bar{D}$(As–OR) with changing R are matched by parallel variations in the values D(H–OR). Empirical evidence suggests that the latter increase as R ascends the series R = Me, Et, Pr, $\mathrm{Bu^t}$ [Murawski, Roberts, and Szwarc, *J. Chem. Physics*, 1951, **19**, 698, give D(H–O–$\mathrm{Bu^t}$) = 106 kcal./mole], implying decreasing resonance stabilization (π-hyperconjugation) in the radicals ·OR of this series. Alternatively expressed, it seems that π-hyperconjugation is strongest in $\cdot\mathrm{O{-}CH_3}$, and decreases with methyl (or alkyl) substitution in the methoxy-group.

THE UNIVERSITY, MANCHESTER, 13.

[*Received, November 27th,* 1952.]