350. *Thermochemistry of Organophosphorus Compounds. Part III.* The Heat of Addition of Sulphur to Triethyl Phosphite, and to Tri-*n*-propyl- and Tri-*n*-butyl-phosphine.*

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The heats of addition of rhombic sulphur to excess of liquid triethyl phosphite, and to liquid tri-*n*-propyl- and tri-*n*-butyl-phosphine have been measured at 25°, $\Delta H_{\text{obs.}} = -26{\cdot}6, -27{\cdot}6$, and $-27{\cdot}5$ kcal./mole respectively. From these heats, and the assumed value ΔH_f° (*S*, g.) $\sim$66 kcal./mole, the heats of disruption of the thiophosphoryl bonds are derived, *viz.* : $D(\text{S}{=}\text{PR}_3)$ $\sim$90·6, 91·6, and 91·5 kcal./mole for R = OEt, Pr^{n}, and Bu^{n} respectively. It is suggested that the degree of multiple bonding (bond order) is less in thiophosphoryl than in phosphoryl bonds.

ACCORDING to Strecker and Spitaler,[1] sulphur adds directly to triethyl phosphite to form triethyl thionophosphate readily at room temperature, $(\text{EtO})_3\text{P} + \text{S} \longrightarrow \text{SP(OEt)}_3$. Kosolapoff[2] states that a similar direct addition occurs with the trialkylphosphines, to form the trialkylphosphine sulphides. In this paper we report on the heats of addition of sulphur to triethyl phosphite and to tri-*n*-propyl- and tri-*n*-butyl-phosphine, measured

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* Part II, *J.*, 1956, 1041.

[1] Strecker and Spitaler, *Ber.*, 1926, **59**, 1772.

[2] Kosolapoff, " Organophosphorus Compounds," John Wiley, New York, 1950, p. 235.

directly from the heat evolved on dissolving pure rhombic sulphur in an excess of each of these liquids.

EXPERIMENTAL

Preparations.—Triethyl phosphite was prepared by the method of Ford-Moore and Perry.[3] The crude product was fractionally distilled under reduced (nitrogen) pressure through an 8″ gauze-packed column. The fraction, b. p. 36·0°/3 mm., was retained. Tri-*n*-propyl- and tri-*n*-butyl-phosphine were prepared according to Davies and Jones [4] and Davies, Pearse, and Jones.[5] The crude products were purified by fractional distillation under reduced (nitrogen) pressure. The fractions retained had b. p. 60—62°/2 mm. (PPr_3) and 68—70°/0·5 mm. (PBu_3). A sample of pure rhombic sulphur was provided by Mr. G. Merrall.

Calorimeter.—The calorimeter will be described in detail elsewhere, and is similar to that used by Chernick, Skinner, and Wadsö.[6] It consists of a Dewar vessel contained in a copper cylindrical can fitted with a flanged lid, and when in use, is totally immersed in a thermostat at 25·0°. A Pyrex-glass reaction vessel (30 ml. capacity) is supported centrally in the Dewar vessel by an arm which emerges through the lid of the calorimeter and attached externally to a Vibro-shaker. The reaction vessel can be vigorously agitated in the water surrounding it inside the Dewar vessel. The procedure in the present experiments was as follows: The reaction vessel was swept out with nitrogen and charged with a known excess of the phosphine derivative. A thin glass ampoule containing a known weight of sulphur was held in position in the reaction vessel. The reaction vessel was then fitted into the calorimeter, and the Vibro-shaker set in oscillation. On attainment of a steady state, the fore-rating curve was plotted from the change in resistance with time of a shielded thermistor element immersed in the water (375 g.) contained in the Dewar vessel. The ampoule was then broken, and the ensuing resistance change plotted until reaction ceased. After this the system re-attained a steady state, and the post-rating curve was plotted.

Reaction between the trialkylphosphines and sulphur is rapid, being complete in <5 min. The sulphur–triethyl phosphite reaction proved more troublesome, for, although reaction begins rapidly, it approaches the end-point sluggishly, and reaction times of 20—30 min. were required. In a few experiments, particles of undissolved sulphur still remained visible in the contents of the reaction vessel at the " end " of the experiment. The results obtained in " unfinished " experiments were discarded.

The calorimeter was calibrated electrically by the substitution method. The experiments were carried out at 25°, and all heat quantities are quoted in thermochemical calories, defined by 1 calorie ≡ 4·1840 abs. joules.

Results.—The observed heats of reaction, $\Delta H_{obs.}$, are given in the following Tables, and relate to the general equation:

$$PR_3\ (liq.) + S(c.) \longrightarrow SPR_3\ (soln.\ in\ PR_3) \quad \ldots\ldots \quad (1)$$

where R = OEt, Pr^n, and Bu^n.

TABLE 1. *Heat of addition of sulphur to triethyl phosphite.*

Expt.	Sulphur (g.)	$-\Delta H_{obs.}$ (kcal./mole)	Expt.	Sulphur (g.)	$-\Delta H_{obs.}$ (kcal./mole)
1	0·5002	26·6	4	0·4018	26·9
2	0·5000	26·2	5	0·3381	27·1
3	0·3780	26·1			

Mean $\Delta H_{obs.} = -26·6 \pm 0·4$ kcal./mole.

TABLE 2. *Heat of addition of sulphur to* PPr_3 *and to* PBu_3.

(a) PPr_3 + S.			(b) PBu_3 + S.		
Expt.	Sulphur (g.)	$-\Delta H_{obs.}$ (kcal./mole)	Expt.	Sulphur (g.)	$-\Delta H_{obs.}$ (kcal./mole)
1	0·3920	27·5	1	0·4124	27·9
2	0·4072	27·6	2	0·3812	26·9
3	0·3930	27·6	3	0·4030	27·7
Mean $\Delta H_{obs.} = -27·6 \pm 0·1$			Mean $\Delta H_{obs.} = -27·5 \pm 0·4$		

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[3] Ford-Moore and Perry, *Org. Synth.*, 1951, **31**, 111.

[4] Davies and Jones, *J.*, 1929, 33.

[5] Davies, Pearse, and Jones, *J.*, 1929, 1262.

[6] Chernick, Skinner, and Wadsö, *Trans. Faraday Soc.*, 1956, **52**, 1088.

DISCUSSION

From the $\Delta H_{\text{obs.}}$ values in Tables 1 and 2, together with certain other thermal data, we may derive values for the heats of disruption of sulphur–phosphorus bonds in SPR_3 molecules. The thermal data required, in addition to $\Delta H_{\text{obs.}}$, are the heats of vaporization of PR_3 and SPR_3, the heats of solution of SPR_3 in liquid PR_3, and the heat of atomization of rhombic sulphur, since :

$$D(S{=}PR_3) = \Delta H_f^{\circ}(\text{S, g.}) - \Delta H_{\text{obs.}} + \Delta H_{\text{vap.}}(PR_3) - \Delta H_{\text{vap.}}(SPR_3) + \Delta H_{\text{soln.}} \quad (2)$$

where $D(S{=}PR_3)$ symbolizes the bond dissociation energy of the sulphur–phosphorus bond in SPR_3.

The heat of formation of atomic sulphur is not yet settled, and several values for it have been proposed. One of the most useful methods of arriving at ΔH_f°(S, g.) is from changes in heat content (ΔH_1 and ΔH_2) of the processes (*a*) and (*b*) respectively :

$$(a)\ \text{S (rhombic)} \longrightarrow S_2\ \text{(g.)};\ \Delta H_1$$

$$(b)\ S_2\ \text{(g.)} \longrightarrow 2\text{S (g.)};\ \Delta H_2$$

whence, ΔH_f°, (S, g.) $= \frac{1}{2}(\Delta H_1 + \Delta H_2)$.

Evans and Wagman [7] concluded that the " best " value for ΔH_1 is 30·8 kcal./mole, obtained from measurements of the dissociation of hydrogen sulphide at high temperatures. The " best " value for ΔH_2 is not easily chosen, and Gaydon [8] considers that there are 3 possible values (3·3, 3·6, and 4·4 ev), from among which he prefers the highest, *i.e.*, $\Delta H_2 = 101$ kcal./mole. On the other hand, a recent investigation by St. Pierre and Chipman [9] led them to conclude that $\Delta H_2 = 83$ kcal./mole.

For the present purpose, we have accepted the values $\Delta H_1 = 30{\cdot}8$ and $\Delta H_2 = 101$, leading to ΔH_f°(S, g.) ~ 66 kcal./mole. Of the remaining items in eqn. (2), data are completely lacking in respect of $\Delta H_{\text{vap.}}(SPR_3)$, and are not well-established in respect of $\Delta H_{\text{vap.}}(PR_3)$, but it is unlikely that the difference, $\Delta H_{\text{vap.}}(SPR_3, \text{liq.}) - \Delta H_{\text{vap.}}(PR_3)$, is appreciably in excess of 2 kcal./mole. The term in $\Delta H_{\text{soln.}}$ is small : in the case of $SPPr_3$, we prepared a pure sample, and measured the heat of mixing with PPr_3, finding $\Delta H_{\text{soln.}}$ to be almost negligible (<0·1 kcal./mole). Hence, we may rewrite eqn. (2) approximately, as :

$$D(S{=}PR_3) \sim 64 - \Delta H_{\text{obs.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

to give :

$$D[S{=}P(OEt)_3] \sim 90{\cdot}6 \text{ kcal./mole}$$
$$D(S{=}PPr_3) \sim 91{\cdot}6 \text{ kcal./mole}$$
$$D(S{=}PBu_3) \sim 91{\cdot}5 \text{ kcal./mole}$$

These values show that the $S{=}PR_3$ bond dissociation energies are markedly less than the related $O{=}PR_3$ dissociation energies, for which values were reported in Part II of this series.[10] Moreover, it would seem that the *increase* in strength of the phosphoryl bond over singly bonded phosphorus to oxygen is *ca.* twice as large as the increase in passing from S–P to S=P. [Chernick, Skinner, and Mortimer [11] obtained $D(P{-}OR) \sim 80$ kcal./mole, and, in Part II, values of $D(O{=}PR_3)$ were found to be >135 kcal./mole. The strength of the P–S single bond has not been measured directly, but can be estimated at *ca.* 64 kcal./mole from the relation between excess of ionic energy (Pauling [12]) and electronegativity difference. Hence the difference between

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[7] Evans and Wagman, *J. Res. Nat. Bur. Stand.*, 1952, **49**, 141.

[8] Gaydon, " Dissociation Energies," Chapman and Hall, London, 1953, p. 205.

[9] St. Pierre and Chipman, *J. Amer. Chem. Soc.*, 1954, **76**, 4787.

[10] Chernick and Skinner, *J.*, 1956, 1401.

[11] Chernick, Skinner, and Mortimer, *J.*, 1955, 3936.

[12] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1939, p. 60.

O=P and O–P is *ca.* 55 kcal./mole, compared with *ca.* 26 kcal./mole between S=P and S–P]. A possible explanation is one that ascribes a greater degree of multiple-bond character to phosphoryl than to thiophosphoryl bonds, and is supported by Siebert's [13] finding, from force-constant measurements, that the O=P bond order in $OPCl_3$ is 2·09 against 1·57 for the S=P bond order in $SPCl_3$. This explanation is in line with a more general suggestion by Baddeley.[14]

Comment was made in Part II on the finding that $D(O=PR_3)$ varies appreciably with changes in the atom, or group, R, and the authors expressed some doubt in respect of the assumptions made in interpreting their thermochemical results. The present study, in contrast, reveals that the $D(S=PR_3)$ values remain almost unchanged on changing the group R, and re-emphasizes the need for an independent verification of the earlier conclusions in respect of phosphoryl bond dissociation energies.

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[13] Siebert, *Z. anorg. Chem.*, 1954, **275**, 210.
[14] Baddeley, *J.*, 1950, 663.