

*Thermochemistry of Organophosphorus Compounds. Part I.
Trimethyl and Triethyl Phosphites.*

By C. L. CHERNICK, H. A. SKINNER, and (in part) C. T. MORTIMER.

[Reprint Order No. 6463.]

Values are reported for the heat of esterification of phosphorus trichloride by methanol and by ethanol in *cyclohexane*. The heats of formation of the trialkyl phosphites are derived, *viz.*, $\Delta H_f^\circ[\text{P}(\text{OMe})_3, \text{liq.}] = -175.0$ and $\Delta H_f^\circ[\text{P}(\text{OEt})_3, \text{liq.}] = -204.1$ kcal./mole.

The mean bond dissociation energies, $\bar{D}(\text{P}-\text{OR})$, are calculated to lie within the range 79–82 kcal./mole.

NEALE and WILLIAMS (*J.*, 1955, 2485) recently studied the thermochemistry of some organophosphorus compounds, making extensive use of reaction calorimetry. We have made similar studies, and acknowledge the advice and assistance given us (from their prior experience) by Neale and Williams. In this paper we report some measurements on the heats of reaction of phosphorus trichloride with methanol, and with ethanol, using essentially the experimental procedure employed by Neale and Williams in their studies of phosphorus trichloride–alcohol reactions. Our value for the heat of formation (ΔH_f°) of triethyl phosphite agrees closely with that given by Neale and Williams; a value for trimethyl phosphite has not previously been given.

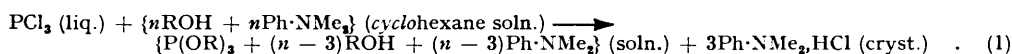
EXPERIMENTAL

Compounds.—Commercial phosphorus trichloride was fractionally distilled in dry nitrogen, and finally in a vacuum into glass ampoules which were then sealed. *cyclo*Hexane (spectroscopic grade) was dried over sodium, and dimethylaniline ("AnalaR") over potassium hydroxide pellets. Ethanol was clinical-grade absolute, and methanol a high-quality synthetic product. Triethyl phosphite was prepared by Ford-Moore and Perry's method (*Org. Synth.*, 1951, 31, 111), and purified by fractional distillation under reduced (nitrogen) pressure through an 8" gauze-packed column; it had b. p. 54.3—54.8°/15 mm.

Calorimeter.—The calorimeter was described by Mortimer and Skinner (*J.*, 1952, 4331). The esterifications were carried out in the Dewar vessel by breaking ampoules containing known weights of phosphorus trichloride under the surface of 750 c.c. of *cyclo*hexane, to which known amounts of alcohol and dimethylaniline had been added. The ensuing temperature changes were followed through the change in resistance of a shielded thermistor element immersed in the solution. The calorimeter was calibrated electrically by the substitution method.

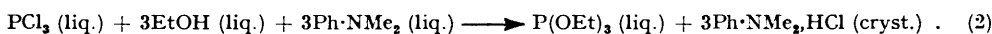
Units.—All heat quantities are given in units of the thermochemical calorie, 1 cal. \equiv 4.1840 abs. joule. The reactions were carried out at 25°.

Results.—The observed heats of reaction ($\Delta H_{\text{obs.}}$) refer to the equation :



where R = Me or Et. For the reactions with ethanol, values of n ranging from 3.3 to 8.0 were used, although in most experiments n was 4.0. For the reactions with methanol, n was 4.0 throughout. The reaction times, with $n = 4$ (or larger), varied somewhat but were generally less than an hour. Reaction to completion was appreciably slower for n values less than 4.

Esterification by Ethanol.—A selection of values of $\Delta H_{\text{obs.}}$ for the ethanol-phosphorus trichloride reaction is given in Table 1. The decrease in $\Delta H_{\text{obs.}}$ for values of $n > 4$ is a consequence of the dependence of the heat of solution of ethanol in *cyclo*hexane on the relative concentrations of the components. Values of the heat of solution of ethanol in ethanol-*cyclo*hexane solutions were measured separately, and are given in Table 2. The heats of solution in *cyclo*hexane of dimethylaniline and triethyl phosphite were also measured independently, and found to be 1.60 and 1.32 kcal./mole, respectively. For the derivation of $\Delta H_f^\circ[\text{P}(\text{OEt})_3, \text{liq.}]$, it is useful to use the $\Delta H_{\text{corr.}}$ values given in the final column of Table 1; these are obtained from $\Delta H_{\text{obs.}}$ on removal of all those heat terms due to the use of *cyclo*hexane solvent, so that $\Delta H_{\text{corr.}}$ is the heat of the idealised reaction :

TABLE 1. Reaction of PCl_3 with excess of ethanol.

PCl_3 (g.)	n (eqn. 1)	$-\Delta H_{\text{obs.}}$ (kcal./mole)	$-\Delta H_{\text{corr.}}$ (kcal./mole)	PCl_3 (g.)	n (eqn. 1)	$-\Delta H_{\text{obs.}}$ (kcal./mole)	$-\Delta H_{\text{corr.}}$ (kcal./mole)
0.6572	4.0	95.0	74.3	0.6313	5.0	95.2	75.3
0.6323	4.0	94.9	74.2	0.6198	7.0	92.7	74.7
0.6991	4.0	95.3	74.6	0.6286	8.0	92.1	76.1

Mean $\Delta H_{\text{corr.}} = -74.8$ kcal./mole.

TABLE 2. Heat of solution of EtOH in *cyclo*hexane-ethanol.

EtOH added (g.)	EtOH present initially (g.)	Ratio initial : finish EtOH	ΔH mixing (kcal./mole of added EtOH)	EtOH added (g.)	EtOH present initially (g.)	Ratio initial : final EtOH	ΔH mixing (kcal./mole of added EtOH)
0.6351	0.21	1 : 4	5.73	0.6276	0.84	4 : 7	4.83
0.6428	0.42	2 : 5	5.47	0.6671	1.11	5 : 8	4.19
0.6232	0.53	2.5 : 5.5	5.25	0.6337	1.16	5.5 : 8.5	4.18
0.6376	0.64	3 : 6	5.01				

Esterification by Methanol.—A selection from the observed heats of reaction is given in Table 3. In these reactions, the amount of alcohol used was adjusted to $n = 4.0$ (eqn. 1) in all cases. The heat of solution of methanol in methanol-*cyclo*hexane for this concentration range was measured separately : $\Delta H_{\text{mixing}} (1 : 4) = 5.70$ kcal. per mole of MeOH added. The heat of solution of trimethyl phosphite in *cyclo*hexane is assumed to be the same as that measured for triethyl phosphite.

TABLE 3. *Reaction of PCl₃ with excess of methanol.*

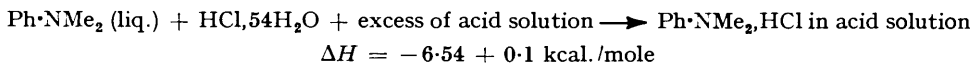
PCl ₃ (g.)	<i>n</i> (eqn. 1)	-Δ <i>H</i> _{obs.} (kcal./mole)	-Δ <i>H</i> _{corr.} (kcal./mole)	PCl ₃ (g.)	<i>n</i> (eqn. 1)	-Δ <i>H</i> _{obs.} (kcal./mole)	-Δ <i>H</i> _{corr.} (kcal./mole)
0.6898	4.0	94.05	73.45	0.7663	4.0	95.15	74.55
0.6399	"	94.2	73.6	0.6335	"	95.0	74.4
0.6390	"	93.6	73.0	0.6124	"	93.5	72.9

$$\text{Mean } \Delta H_{\text{corr.}} = -73.7 \text{ kcal./mole.}$$

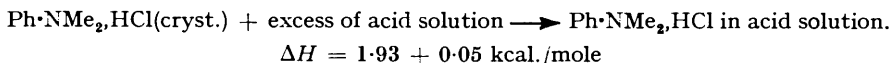
Heats of Formation.—The heats of formation of the alkyl phosphites are related to the corresponding Δ*H*_{corr.} through the thermochemical equation :

$$\Delta H_f^\circ[\text{P(OR)}_3, \text{liq.}] = \Delta H_{\text{corr.}} + \Delta H_f^\circ(\text{PCl}_3, \text{liq.}) + 3\Delta H_f^\circ(\text{ROH}, \text{liq.}) + 3\{\Delta H_f^\circ(\text{Ph}\cdot\text{NMe}_2, \text{liq.}) - \Delta H_f^\circ(\text{Ph}\cdot\text{NMe}_2, \text{HCl}, \text{cryst.})\} \quad (3)$$

The difference Δ*H*_f^o(Ph·NMe₂, liq.) - Δ*H*_f^o(Ph·NMe₂, HCl, cryst.) was measured in the following manner. Dimethylaniline was dissolved in excess of *n*-hydrochloric acid :



The heat of solution of crystalline dimethylaniline hydrochloride in excess of *n*-hydrochloric acid was also measured directly :



Whence, using Δ*H*_f^o(HCl, 54H₂O) = -39.60 kcal./mole (Nat. Bur. Stand. Tables, Circular 500), we derive for the difference required, 48.07 ± 0.08 kcal./mole. Of the remaining terms in eqn. (3), Δ*H*_f^o(EtOH, liq.) = -66.36 kcal./mole and Δ*H*_f^o(MeOH, liq.) = -57.04 kcal./mole are well-established (*op. cit.*): the value Δ*H*_f^o(PCl₃, liq.) = -74.4 kcal./mole, recently obtained by Neale and Williams (*J.*, 1954, 2156), is accepted here. Accordingly, from the mean Δ*H*_{corr.} values in Tables 1 and 3, and eqn. (3), we derive : Δ*H*_f^o[P(OMe)₃, liq.] = -175.0 kcal./mole, and Δ*H*_f^o[P(OEt)₃, liq.] = -204.1 kcal./mole. The absolute limits of error to be attached to these values are difficult to assess, since the accepted value for Δ*H*_f^o(PCl₃, liq.) is itself subject to possible error latent in the heat of formation of phosphoric acid. The experimental errors in our Δ*H*_{corr.} values we would assess at *ca.* ±1 kcal./mole.

Discussion.—The value of Δ*H*_f^o[P(OEt)₃, liq.] reported here is in good agreement (within the error limits of the individual determinations) with that given by Neale and Williams (*loc. cit.*). It may also be remarked that the difference between the heats of formation of liquid trimethyl phosphite and triethyl phosphite (29.1 kcal./mole) is of similar magnitude to the difference between the heats of formation of liquid trimethyl and triethyl arsenites (27.5 kcal./mole; Charnley, Mortimer, and Skinner, *J.*, 1953, 1181), and between the heats of formation of liquid trimethyl and triethyl borates (27.3 kcal./mole; Charnley, Skinner, and Smith, *J.*, 1952, 2288).

The mean bond dissociation energies $\bar{D}(\text{P-OR})$ [defined as one-third of the heat required to dissociate one mole of gaseous P(OR)₃ into gaseous P atoms and ·OR radicals] may be calculated from the heats of formation, in conjunction with the following subsidiary thermal data : Δ*H*_f^o(P, g.) = 75.2 kcal./mole (*op. cit.*), Δ*H*_f^o(·OMe, g.) = -1.3 ± 2 kcal./mole, Δ*H*_f^o(·OEt, g.) = -8.1 ± 1 kcal./mole (Charnley, Mortimer, and Skinner, *loc. cit.*), and Δ*H*_{vap.}[P(OMe)₃] = 8.8 kcal./mole, Δ*H*_{vap.}[P(OEt)₃] = 10.0 kcal./mole (estimated from vapour-pressure data in the literature). We obtain $\bar{D}(\text{P-OMe}) = 79.2$ and $\bar{D}(\text{P-OEt}) = 81.7$ kcal./mole. Gray (*Proc. Roy. Soc.*, 1954, 221, A, 462) has recently given slightly different values from the above for the heats of formation of ·OMe and ·OEt radicals, *viz.*, Δ*H*_f^o(·OMe, g.) = -0.5 and Δ*H*_f^o(·OEt, g.) = -9.0 kcal./mole. With these values we obtain 80.0 and 80.8 kcal./mole, respectively, for $\bar{D}(\text{P-OMe})$ and $\bar{D}(\text{P-OEt})$.

The authors are glad to acknowledge the assistance and advice given them by Mr. L. T. D. Williams and Mr. E. Neale.