90. *The Heats of Hydrolysis of Some Halides and Oxyhalides of Phosphorus.*

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The heats of hydrolysis (at 25°) of liquid PCl_3, PBr_3, $POCl_3$, and crystalline $POBr_3$ have been measured, from which the respective heats of formation ($\Delta Hf°$) are derived as follows: −79·4, −46·5, −143·8, and −110·1 kcal./mole. Values of the *mean* bond dissociation energies, $\bar{D}$(P–Cl) = 77·9 and $\bar{D}$(P–Br) = 63·4 kcal./mole in PCl_3 and PBr_3 are calculated, and the P–O bond dissociation energies in the oxyhalides are: $D(O{=}PCl_3)$ = 121·8 and $D(O{=}PBr_3)$ = 119·3 kcal./mole.

NEALE and WILLIAMS (*J.*, 1952, 4535) have recently measured the heats of hydrolysis of phosphorus trichloride and oxychloride, obtaining significantly larger values than those due to Thomsen ("Thermochemische Untersuchungen," 1882, Vol. 2) and to Berthelot and Louguinine (*Ann. Chim. Phys.*, 1875, **6**, 305). The present studies were undertaken partly as an independent check on Neale and Williams's results, and more generally as a revision of the older thermal data on the halides and oxyhalides of phosphorus.

EXPERIMENTAL

(a) *Preparation of Compounds.*—Commercial samples of phosphorus trichloride, tribromide, and oxychloride were fractionated in nitrogen, and finally distilled into thin-glass ampoules in an all-glass, greaseless, vacuum system. Commercial phosphorus oxybromide was recrystallised from anhydrous ether, and purified by sublimation in a high vacuum.

(b) *The Calorimeter.*—This was a 1-l. narrow-necked Dewar vessel, as described by Charnley, Skinner, and Smith (*J.*, 1952, 2288). The experiments were carried out by breaking the ampoules under the surface of 750 g. of distilled water contained in the Dewar vessel, and following the resultant temperature changes in terms of the change in resistance of a shielded thermistor element immersed in the solution. Calibration of the calorimeter was done electrically, by the substitution method.

These hydrolyses proceed at a moderate speed only, requiring in some cases upwards of 30 min. to reach completion. Time–temperature curves with fore- and after-rating periods of at least 60 min. were taken in making due allowance for heat losses during the experiments.

All results are given in terms of the thermochemical calorie, 1 cal. = 4·1840 abs. joule. Experiments were carried out at 25°. The observed heats—quoted under $\Delta H_{obs.}$ in the tables of results—refer, in the case of the trihalide hydrolyses, to the reactions

$$PX_3\,(liq.) + (n + 3)H_2O\,(liq.) \longrightarrow [H_3PO_3 + 3HX] \text{ in } nH_2O\,(liq.) \quad . \; . \; . \quad (1)$$

and in the case of the oxyhalides to the reactions

$$POCl_3\,(liq.) + (n + 3)H_2O\,(liq.) \longrightarrow [H_3PO_4 + 3HCl] \text{ in } nH_2O\,(liq.) \quad . \; . \; . \quad (2)$$

and

$$POBr_3\,(cryst.) + (n + 3)H_2O\,(liq.) \longrightarrow [H_3PO_4 + 3HBr] \text{ in } nH_2O\,(liq.) \quad . \; . \quad (3)$$

The derived heats of formation, $\Delta Hf°$, make use of subsidiary thermochemical data on the heats of formation of water and of aqueous solutions of hydrogen chloride and bromide and of phosphorous and phosphoric acid. These assumed data were taken from the " Selected Values of Chemical Thermodynamic Properties," compiled by the National Bureau of Standards, Washington (Circular 500).

Results.—The results obtained are summarised in Table 1. We add the following comments : (*a*) PCl_3 : The mean value, $\Delta H_{obs.} = -67·7 \pm 0·5$ kcal./mole is in close agreement with the vale ($\Delta H = -67·5$ kcal./mole) obtained by Neale and Williams (*loc. cit.*). Thomsen's earlier value (*loc. cit.*) was $\Delta H = -65·1$ kcal/mole. (*b*) PBr_3 : Berthelot and Louguinine (*loc. cit.*) gave $\Delta H = -64·0$ kcal./mole, compared with our mean value $\Delta H_{obs} = -67·2 \pm 0·6$ kcal./mole. (*c*) $POCl_3$: Thomsen found $\Delta H = -72·2$ and Berthelot $-74·6$ kcal./mole. Neale and Williams's value ($\Delta H = -79·9$) is in much better agreement with the present mean, *viz.*, $\Delta H_{obs.} = -80·4 \pm 0·4$ kcal./mole. (*d*) $POBr_3$: Ogier (*Compt. rend.*, 1881, **92**, 83) reported $\Delta H = 79·7$ kcal./mole for the heat of hydrolysis of crystalline $POBr_3$. The present mean value is $\Delta H_{obs.} = -80·8 \pm 0·5$ kcal./mole.

The older measurements of these hydrolysis heats were made at lower temperatures and in more concentrated solutions than the measurements now reported. Part of the discrepancy between the old and the new results is due to these causes.

TABLE 1.

Expt.	Wt. (g.)	*n* (moles)	$\Delta H_{obs.}$ (kcal.)	$\Delta Hf°$ (kcal.)	Expt.	Wt. (g.)	*n* (moles)	$\Delta H_{obs.}$ (kcal.)	$\Delta Hf°$ (kcal.)
	Reactant : PCl_3 (liq.).					Reactant : $POCl_3$ (liq.).			
1	0·7160	7,990	−67·0	−80·1	1	2·3484	2,720·	−80·5	−143·6
2	1·1172	5,120	−68·0	−79·0	2	1·5674	4,070	−80·5	−143·6
3	0·7735	7,400	−67·3	−79·8	3	1·2213	5,230	−80·8	−143·4
4	1·3470	4,250	−67·8	−79·2	4	2·0604	3,100	−80·2	−143·9
5	0·6328	9,040	−68·1	−79·0	5	2·1465	2,970	−80·2	−143·9
6	0·6950	8,230	−68·0	−79·1	6	2·4066	2,650	−80·3	−143·8
	Mean values :		−67·7	−79·4		Mean values :		−80·4	−143·8
	Reactant : PBr_3 (liq.).					Reactant : $POBr_3$ (cryst.).			
1	2·7676	4,070	−66·8	−46·85	1	1·7698	6,740	−80·7	−110·2
2	1·2966	8,700	−67·3	−46·45	2	1·7512	6,815	−80·9	−110·0
3	2·6468	4,240	−67·8	−45·9	3	0·9634	12,390	−81·2	−109·8
4	2·1972	5,130	−66·6	−47·1	4	3·3728	3,540	−80·6	−110·1
5	0·9303	12,095	−67·6	−46·2	5	1·5552	7,670	−80·7	−110·2
	Mean values :		−67·2	−46·5		Mean values :		−80·8	−110·1

DISCUSSION

The values of $\Delta Hf°$ given in Table 1 refer to the *liquid* state in case of phosphorus trichloride, tribromide, and oxychloride, and to the *crystalline* state of phosphorus oxybromide. The errors in these $\Delta Hf°$ include the experimental errors in $\Delta H_{obs.}$, and errors present in the assumed thermal data. Of these, the errors in $\Delta Hf°$ (H_2O, liq.) and $\Delta Hf°$(HCl, aq.) are small ($\pm 0·010$ and $\pm 0·040$ kcal./mole, respectively). The errors in $\Delta Hf°(H_3PO_3$, aq.) and $\Delta Hf°(H_3PO_4$, aq.) may, however, be more significant. The National Bureau of Standards recommended value, $\Delta Hf°(H_3PO_4$, cryst.) $= -306·2$ kcal./mole, is derived from a series of experiments by Thomsen (*loc. cit.*), the overall accuracy of which is difficult to assess; some independent measurements by Giran (*Ann. Chim. Phys.*, 1903, **30**, 203) confirm Thomsen's value, so that in this case one might accept the chosen value with some degree of confidence. The value $\Delta Hf°$ (H_3PO_3, cryst.) $= -232·2$ kcal./mole is also derived from a series of data due to Thomsen, but in this case confirmatory evidence is lacking and the accuracy of the value is a matter for speculation. The *overall* error limits in $\Delta Hf°$ values now reported cannot therefore be given in a strict manner : in the case of the oxyhalides [involving $\Delta Hf°$ (H_3PO_4)], they should not exceed ± 1 kcal./mole. The conversion of the $\Delta Hf°$ of Table 1 into gaseous-state values in Table 2 makes use of the heats of vaporisation ($\lambda_{vap.}^{25}$) given in the N.B.S. Circular 500. The heat of sublimation of solid phosphorus oxybromide is an estimate.*

* The N.B.S. tables give $\lambda_{vap.}^{192} = 9·1$ kcal./mole. The corresponding value at 25°, we estimate at 11·5—12 kcal. To this is added an estimated heat of fusion of 3—4 kcal., leading to $\lambda_{sub.} = 15 \pm 1$ kcal.

Values given under $\bar{D}$(P–X) in Table 2 are the calculated *mean* bond dissociation energies* of P–X bonds in PX_3. In the final column, the values given are of the $O{=}PX_3$ bond dissociation energies. The $\bar{D}$ values differ from those given by Pauling ("Nature of the Chemical Bond," p. 53, 1940, Cornell Univ. Press), partly through the changes in $\Delta Hf°(PX_3)$,

TABLE 2.

Molecule	$\Delta Hf°$	λ^{25}	$\Delta Hf°$ (g.)	$\bar{D}$(P–X)	$D(O{=}PY_3)$
PCl_3 (liq.)	− 79·4	7·8	− 71·6	77·9	—
PBr_3 (liq.)	− 46·5	11·6	− 34·9	63·4	—
$POCl_3$ (liq.)	−143·8	9·5	−134·3	—	121·8
$POBr_3$ (cryst.)	−110·1	15	− 95·1	—	119·3
POF_3	—	—	—	—	129·8

but mainly by the adoption of the value for $\Delta Hf°$ (P, g.) given in the N.B.S. tables (75·18 kcals.). The value given for $D(O{=}PF_3)$ is derived from Ebel and Bretscher's data (*Helv. Chim. Acta*, 1929, **12**, 450), who measured the heat of oxidation of PF_3 directly.

The structure of POX_3 may be formulated either as $O{=}PX_3$, or as $O{\leftarrow}PX_3$: both structures may represent extremes from which a resonance hybrid is constructed, but it is of interest to consider which structure is the dominating one. Phillips, Hunter, and Sutton (*J.*, 1945, 146) have discussed this point, concluding from the evidence of dipole moments and bond-lengths, that the O–P bonds in POX_3 resemble double, rather than single bonds. The bond-energy data point in the same direction.

A reliable evaluation of the energy of the single-bonded P–O link cannot yet be made. Recently, Koerner and Daniels (*J. Chem. Physics*, 1952, **20**, 113) reported a measurement of the heat of formation of liquid P_4O_6, from which we have derived $\Delta Hf°(P_4O_6, g.) = -530$ kcal./mole, and $\bar{D}$(P–O) = 98·8 kcal./mole. Their value was obtained by an indirect experimental method, and for this reason requires confirmation. The P–O bond strength range of 120—130 kcal./mole in POX_3 lies well above the single-bonded $\bar{D}$(P–O) value, and is consistent with a considerable degree of double-bonded character in the $O{-}PX_3$ linkages.

The decrease in $D(O{=}PX_3)$ as X changes through F ⟶ Cl ⟶ Br follows the order that might be expected if steric repulsion forces between the X_3 grouping and the O atom were appreciable. Williams, Sheridan, and Gordy (*J. Chem. Physics*, 1952, **20**, 164) found, however, the same bond-length for P–O (1·45 Å) in POF_3 as in $POCl_3$, and the simple steric explanation of the variations in $D(O{=}PX_3)$ seems inadequate.

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* $\bar{D}$(P–X) is one-third of the heat of atomization of PX_3 (gas) into normal gaseous atoms. The $\Delta Hf°$ of the atoms are from the N.B.S. tables.