118. *Thermochemistry of Phosphorus Iodides.*

By Arthur Finch, P. J. Gardner, and I. H. Wood.

The enthalpy of formation of phosphorus tri-iodide has been measured by aqueous hydrolysis, and a value of −10·7 ± 0·4 kcal. mole^{-1} has been obtained. The solution enthalpies of phosphorus tri-iodide and diphosphorus tetraiodide in carbon disulphide are also reported as 4·09 ± 0·02 and 6·0 ± 0·1 kcal. mole^{-1}, respectively.

The current literature values [1] for the standard enthalpy of formation of phosphorus tri-iodide derive from two very early determinations. These involve (i) the synthesis from the elements in an unspecified small quantity of solvent and (ii) the alkaline hydrolysis to potassium phosphite. The values obtained by these methods, −10·9 and −10·5 kcal. mole^{-1}, respectively, are apparently in very good agreement. However, there is reason to doubt whether the concordance is real since, (*a*) in method (i) no allowance was made for a solution enthalpy term, and it is also probable that the solvent system was impure and, (*b*) the stoicheiometry of the alkaline hydrolysis of method (ii) is questionable. Both reasons (*a*) and (*b*) are amplified in the Discussion section. It was therefore decided to investigate a further degradation procedure. Results for the solution enthalpy of diphosphorus tetraiodide are also recorded.

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[1] Hartley, Holmes, Jacques, Mole, and McCoubrey, *Quart. Rev.*, 1963, **27**, 204.

EXPERIMENTAL

Preparation of Iodides.—These were synthesised from the elements in carbon disulphide under an inert atmosphere according to the method of Germann and Traxler;[2] phosphorus tri-iodide was recrystallised from a minimum volume of pure carbon disulphide and the tetraiodide from purified chlorobenzene [phosphorus tri-iodide, m. p. 61° (lit. m. p. 61°); diphosphorus tetraiodide, m. p. 124·5° (lit. m. p. = 124—125°)].

Purification of Carbon Disulphide.—A commercial sample (B.D.H. AnalaR) was successively shaken with aqueous potassium permanganate, calcium chloride, and mercury, followed by fractional distillation immediately before use. When the solvent was used for calorimetry, dry nitrogen was passed through it for 20 min. immediately before the calorimeter was loaded. This procedure was essential for experiments involving the sub-iodide.

Calorimeter.—A constant-temperature-environment glass Dewar type of calorimeter[3] was used, totally immersed in a thermostat at 25 ± 0·01°. Calibration was electrical and temperature differences were measured by means of an F53 thermistor (Standard Telephones and Cables Ltd.). In addition, temperature changes were monitored with a miniature platinum-resistance thermometer coupled to a six-inch potentiometric recorder; the trace of the latter was used to estimate thermal leakage.

Units.—All thermal values are given in terms of the thermochemical calorie defined as 1 cal. = 4·1840 abs. joules.

The enthalpy of aqueous hydrolysis (ΔH_{obs}) of the following reaction was measured

$$PI_3(\text{cryst}) + (n + 3)\ H_2O(\text{liq}) = [H_3PO_3 + 3HI]nH_2O\ \Delta H_{\text{obs}}$$

Using a value (−227·1 kcal. mole⁻¹) calculated by Hartley *et al.* for ΔH_f° H_3PO_3(aq), and data from N.B.S. Circular 500 for ΔH_f° $HInH_2O$ and ΔH_f° H_2O (liq), we have derived a value of ΔH_f° PI_3 (cryst) from the following equation

$$\Delta H_f^\circ\ PI_3(\text{cryst}) = \Delta H_f^\circ\ H_3PO_3nH_2O + 3\Delta H_f^\circ\ HInH_2O - 3\Delta H_f^\circ\ H_2O(\text{liq}) - \Delta H_{\text{obs}}$$

Table 1 records the values of ΔH_{obs} where N is the ratio of the number of moles of water to phosphorus tri-iodide and T is the mean temperature of the reaction period.

TABLE 1.

Observed enthalpies of aqueous hydrolysis of phosphorus tri-iodide.

Expt.	N	T (°c)	ΔH_{obs} (kcal. mole⁻¹)	ΔH_f° PI_3 (cryst.)
1	3135	25·4	−55·0 *	
2	1467	25·7	−52·0 *	
3	995	25·9	−51·0	−10·8
4	915	26·4	−51·4	−10·4
5	687	26·3	−50·9	−10·9
6	478	27·4	−50·9	−10·8
			Mean value (kcal. mole⁻¹)	−10·7 ± 0·4

* For an interpretation of these anomalous values, see Discussion.

Values for the enthalpies of solution of phosphorus tri-iodide and diphosphorus tetraiodide in carbon disulphide are shown in Tables 2 and 3.

TABLE 2.

Enthalpies of solution of phosphorus tri-iodide in carbon disulphide.

Expt.	N	T	ΔH_s
1	359	24·7	+4·11
2	200	24·7	+4·07
	Mean value (kcal. mole⁻¹)		+4·09 ± 0·02

TABLE 3.

Enthalpies of solution of diphosphorus tetraiodide in carbon disulphide.

Expt.	N	T	ΔH_s
1	525	24·8	+5·9
2	429	24·7	+6·1
	Mean value (kcal. mole⁻¹)		+6·0 ± 0·1

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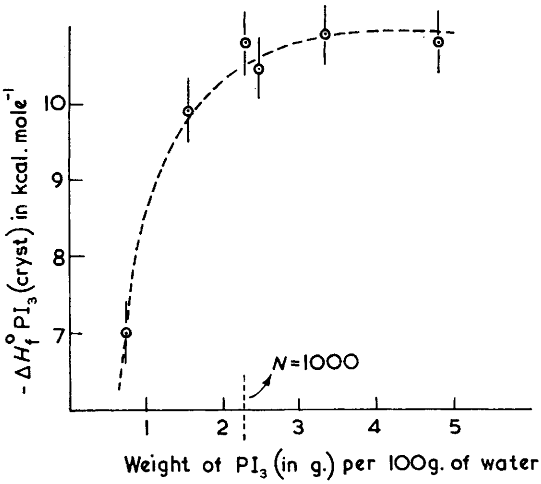
[2] Germann and Traxler, *J. Amer. Chem. Soc.*, 1927, **49**, 307; *J. Phys. Chem.*, 1925, **29**, 1119.

[3] Finch and Gardner, *J.*, 1964, 2985.

DISCUSSION

Comparison with Previous Work.—(a) *Enthalpies of solution.* The values reported in this work for the enthalpies of solution, ΔH_s, of phosphorus tri-iodide and phosphorus tetraiodide are 4·09 ± 0·02 and 6·0 ± 0·1 kcal. mole^{-1}, respectively. The corresponding results in the literature, due to Ogier, are +3·3 and *ca.* −5·0 kcal. mole^{-1}, respectively. The latter value is clearly considerably in error, since the solution process is apparently exothermic, presumably because of reaction of the phosphorus tetraiodide with oxygen or sulphur. In the present work it was found that, in the absence of precautions to exclude oxygen, dissolution was also exothermic, and a film of red-yellow amorphous solid was deposited on the calorimeter walls and inserts. This is in accord with recently reported[4] results on the relatively rapid reaction of diphosphorus tetraiodide with oxygen to form a polymer of approximate composition $[P_3I_2O_6]_n$. This renders suspect the literature value of ΔH_f° P_2I_4 (cryst.), since this was determined from the same source by a synthetic procedure also by using carbon disulphide. This is unfortunate, since it is difficult to devise a suitable and alternative degradative method, and values of thermodynamic functions of diphosphorus tetraiodide would be of considerable interest, because simple compounds containing a P–P bond are rare.



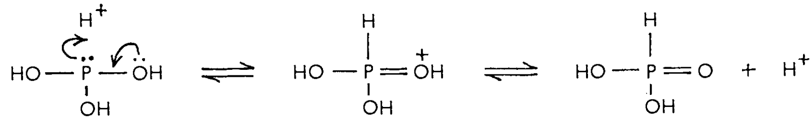
Variation of ΔH_f° PI_3(cryst.) with weight of PI_3 taken per 100 g. of water.

(b) *Standard enthalpy of formation of phosphorus tri-iodide.* Values of ΔH_f° PI_3(cryst.) determined from the present work, by a synthetic method[5] (Ogier), and from an alkaline hydrolysis experiment,[1] are respectively −10·7 ± 0·4, −10·9, and −10·5 kcal. mole^{-1}. In Ogier's synthetic method, a " small " amount of carbon disulphide was used. The results were not corrected for the enthalpy of solution of phosphorus tri-iodide in carbon disulphide, ΔH_s. Since the solubility of phosphorus tri-iodide in carbon disulphide is high, and ΔH_s $PI_3(CS_2)$ = 4·1 kcal. mole^{-1}, the correction would probably be appreciable, and hence the apparent agreement between Ogier's results and those of the other determinations is probably fortuitous. A similar argument does not apply to the " synthetic " determination of ΔH_f° P_2I_4(cryst.), since the latter compound is much less soluble in carbon disulphide. In neither case do reported experimental details suffice for correction to be made. The close agreement between the present results and those of Bertholet is also surprising in view of the doubtful existence of potassium phosphite, K_3PO_3.

Variation of ΔH_f° *PI_3(cryst.) Values.*—The divergence of values of ΔH_f° PI_3(cryst.) at high molar ratios of solvent to solute is illustrated in the Figure. This is possibly due to

[4] Baudler and Fricke, *Z. anorg. Chem.*, 1963, **319**, 211.

the existence of two forms of phosphorous acid, H_3PO_3, *viz.* $P(OH)_3$ the α-form, and $(H)(O)P(OH)_2$, the β-form, *i.e.* the hydrolysis reaction may be represented by $PI_3(cryst) + (n + 3)\ H_2O(liq) = \left[\frac{1}{x}(H)(O)P(OH)_2 + \left(1 - \frac{1}{x}\right)P(OH)_3 + HI\right]nH_2O$, and $x \longrightarrow 1$ as $N \longrightarrow$ about 1000. The stable existence of a three-co-ordinate phosphorus acid (α-form) in aqueous solution, has received much discredit in the literature,[6] although there have been comparatively recent attempts to synthesise this modification.[7] Simon and Schulze[8] have studied the tautomeric equilibrium of phosphorus acid in aqueous solution by deuterium exchange and conclude " that both tautomeric forms of H_3PO_3 exist, but the concentration of the form $P(OH)_3$ is negligible." Mitchell[9] interprets the results of a kinetic study on the oxidation of phosphite to phosphate by halogens in the form of the rate-determining step being $\beta\text{-}H_3PO_3 \longrightarrow \alpha\text{-}H_3PO_3$. A more relevant study of the co-existence of the isomeric forms is that of Kolitowska,[10] who investigated the extent to which either modification is individually produced in the aqueous hydrolysis of phosphorus trichloride, tribromide and tri-iodide. The different forms were distinguished assuming that mild oxidation of the α-form yields hypophosphoric acid ($H_4P_2O_6$), while similar oxidation of the β-form yields phosphoric acid (H_3PO_4). The quantitative estimation of the hypophosphoric acid obtained is a measure of the $\alpha\text{-}H_3PO_3$ yield in the phosphorus halide hydrolysis. Kolitowska finds that the ratio of α- and β-forms depends on, (*a*) the particular halide, (*b*) the pH value of the system (kept approximately constant by the use of suitable buffers), and (*c*) the temperature of hydrolysis. In particular, the following results of Kolitowska are relevant: (*a*) aqueous hydrolysis of phosphorus tri-iodide at 0° produces about 38% of $\alpha\text{-}H_3PO_3$, very nearly independently of pH, (*b*) the effect of raising the temperature from 0 to 25° [with PBr_3] has a minor effect on the yield of the α-form and, (*c*) the concentration of $\alpha\text{-}H_3PO_3$ formed on hydrolysis of PCl_3 is low. In connection with (*a*) it is worthy of note that the highest hydrogen-ion concentration investigated by Kolitowska corresponded to pH 3·5, whereas in the experiments reported here the pH at $N \sim 1000$ is about 0·8. Undoubtedly, the configuration $sp^3(\pi^2)$ is more stable than sp^3 at the phosphorus atom so that the β-form appears to be the preferred modification. However, if the hydrolysis mechanism of PX_3 (X = halogen) is considered in terms of consecutive nucleophilic substitutions, it is likely that the form $P(OH)_3$ will have at least a transitory existence. If the equilibrium between the two forms, in aqueous solution, is written



$$HO-\ddot{P}(OH)-OH + H^+ \rightleftharpoons HO-P(H)(OH)=\overset{+}{O}H \rightleftharpoons HO-P(H)(OH)=O + H^+$$

α β

it is possible that at high hydrogen-ion concentration, the equilibrium lying to the right hand side is far more rapidly attained than at lower acid concentrations. At these lower concentrations (pH 0·8), the equilibrium is slowly attained, the resultant uncertainty in the final thermochemical state giving rise to anomalous values for ΔH_{obs}.

From the experimental data of Table 1, it is apparent that $\Delta H(\alpha \longrightarrow \beta)$ is endothermic. If the β-form is thermodynamically more stable than the α-form [*i.e.*, $\Delta G(\alpha \longrightarrow \beta) < 0$], then the entropy change is the controlling factor in the equilibrium. The existence of the two modifications of phosphorus acid on the hydrolysis of PX_3 introduces an ambiguity

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[5] Ogier, *Compt. rend.*, 1881, **92**, 83.

[6] Van Wazer, " Phosphorus and its Compounds," Interscience New York, 1958; Mellor, " A Comprehensive Trentise on Inorganic and Theoretical Chemistry," Longmans, 1928.

[7] Voigt, *Bull. Soc. chim. France*, 1953, 212.

[8] Simon and Schulze, *Z. anorg. Chem.*, 1958, **296**, 287.

[9] Mitchell, *J.*, 1923, **123**, 2241; 1924, **125**, 1013; 1925, **127**, 336.

[10] Kolitowska, *Roczniki Chem.*, 1953, **27**, 191.

in the current literature value for ΔH_f° H_3PO_3(cryst) obtained from a thermochemical study of the hydrolysis of phosphorus trichloride. However, Kolitowska's evicence [see point (*c*) above] suggests this may not be an important factor. The order of magnitude of the reorganisation energy involved in the isomeric change $H_3PO_3(\alpha) \longrightarrow H_3PO_3(\beta)$ is evaluated in the Appendix.

In an attempt to resolve the ambiguity of the final thermochemical state, an oxidative hydrolysis of phosphorus tri-iodides in an excess of aqueous bromine was investigated. In this case, the final product is phosphoric acid, for which reliable data are available. The reaction studied is

$$PI_3(\text{cryst}) + [5/2\ Br_2 + 4H_2O]nH_2O = [H_3PO_4 + 5HBr]nH_2O + 3I_2(c)$$

Iodine is not appreciably soluble in water and the further reaction must be considered

$$I_2(c) + HBr\ aq \longrightarrow [I_2Br^- + H^+]\ aq.$$

Unfortunately, the results of this investigation are inconclusive (see Table 4).

TABLE 4.

Enthalpies of hydrolysis of phosphorus tri-iodide by aqueous bromine.

Expt.	N *	T	ΔH_{obs} (kcal. mole^{-1})
1	6186	25·0	−186·2
2	4363	25·3	−182·3
3	3220	26·1	−179·2
4	2197	26·8	−175·0

* With respect to H_2O.

Values of ΔH_f° derived from the above figures vary linearly with concentration. A theoretical evaluation of the enthalpy change of the oxidation reaction at $N = 4000$ and $T = 25°$, by using data from a standard reference,[11] ΔH_f° PI_3(cryst) from hydrolysis experiments reported here, ΔH_f° [H_3PO_3(aq) and H_3PO_4(aq)] from Hartley[1] and Lee and Lee's[12] results for dissolution of I_2(cryst) in HBr (aq) gives a value of −171 kcal. mole^{-1}.

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APPENDIX

Estimation of the reorganisation enthalpy $\Delta H_r(g)$ between α- and β-phosphorous acid in the gas phase.

The energy associated with the process:

$$\underset{sp^3}{P(OH)_3(g)} \longrightarrow \underset{sp^3(\pi^2)}{(H)(O)P(OH)_2}\ \Delta H_r(g)$$

is, in terms of bond energies:

$$\Delta H_r = E(P\text{–}H) - E(P\text{–}OH) + E(P\text{=}O)$$

Evaluation of this expression from literature tabulations of bond energies assumes that the P–OH retains the same characteristics independently of the hybridisation at the phosphorus atom. A more realistic estimate of part of the expression [E(P–H) − E(P–OH)] may be obtained by considering the following thermochemical cycle.

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[11] Rossini *et al.*, Nat. Bur. Standards, Circular 500, 1952.

[12] Lee and Lee, *J. Chinese Chem. Soc.*, 1936, **4**, 126.

$$\begin{tikzcd}
\tfrac{1}{4}\mathrm{P_4(cryst)} \arrow[d] & + & n\mathrm{O_2(g)} \arrow[d] & + & \tfrac{3}{2}\,\mathrm{H_2(g)} \arrow[d] \arrow[r, "\Delta H_f^\circ"] & \left.\begin{matrix} \mathrm{H_3PO_3}(n = 3/2) \\ \text{or} \\ \mathrm{H_3PO_4}(n = 2)\end{matrix}\right\}\text{(cryst)} \arrow[d, "\Delta H_{\text{vap}}"] \\
\mathrm{P(g)} & + & 2n\mathrm{O(g)} & + & 3\mathrm{H(g)} & \left.\begin{matrix}\mathrm{H_3PO_3}\\ \text{or}\\ \mathrm{H_3PO_4}\end{matrix}\right\}\text{(g)} \arrow[l, "\Sigma E"']
\end{tikzcd}$$

from which
$$\Sigma E(\mathrm{H_3PO_3}\beta) = 2E(\mathrm{P{-}OH}) + E(\mathrm{P{=}O}) + E(\mathrm{P{-}H})$$
$$\Sigma E(\mathrm{H_3PO_4}) = 3E(\mathrm{P{-}OH}) + E(\mathrm{P{=}O})$$

it being assumed that $\Delta H_{\text{vap}}(\mathrm{H_3PO_3}\text{-}\beta) \doteqdot \Delta H_{\text{vap}}(\mathrm{H_3PO_4})$

$$\begin{aligned}\Sigma E(\mathrm{H_3PO_3}\text{-}\beta) - \Sigma(\mathrm{H_3PO_4}) &= E(\mathrm{P{-}H}) - E(\mathrm{P{-}OH}) \\ &= \Delta H_f^\circ\ \mathrm{O(g)} - \Delta H_f^\circ\ \beta\text{-}\mathrm{H_3PO_3}\ \text{(cryst)} + \Delta H_f^\circ\ \mathrm{H_3PO_4}\ \text{(cryst)} \\ &= 59{\cdot}55\,\dagger + 227{\cdot}1\,{*} - 305{\cdot}7\,{}^{1} \\ &\doteqdot -19\ \text{kcal.}\end{aligned}$$

A molecule with a formally similar structure to H_3PO_4 is $(EtO)_3PO$ for which $E(P{=}O)$ is 151 kcal.[1]. Combining this figure with the above values we have $\Delta H_r = 132$ kcal. mole^{-1}. It appears, then, that both in solution and in the gas phase $\Delta H(\alpha \longrightarrow \beta)$ is endothermic.

* The value quoted in reference (1) is ΔH_f° H_3PO_3(aq); however experiment shows ΔH_s° (H_3PO_3) $< 0{\cdot}3$ kcal. mole^{-1}.

† See ref. 13.

[13] Lewis and Randall, " Thermodynamics," 2nd edn., McGraw Hill, New York, 1961.