The Standard Enthalpies of Hydrolysis and Formation of Tricyanophosphine

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By use of a solution calorimeter the standard enthalpy of hydrolysis of $P(CN)_3(c)$ at 298.15 K has been determined as -44.9 ± 0.1 kcal mol^{-1} and the derived standard enthalpy of formation as 117.9 ± 6.0 kcal mol^{-1}. The enthalpy of sublimation of $P(CN)_3$ was determined by effusion manometry as 18.0 ± 0.7 kcal mol^{-1} and the P–CN mean bond dissociation energy was estimated as 84 kcal mol^{-1}.

ALTHOUGH the heats of formation of the trihalogenophosphines are well established [1,2] corresponding data for the pseudohalides of phosphorus are unknown. This paper describes the calorimetric determination of the heat of hydrolysis of one such pseudohalide, tricyanophosphine, and the determination of its vapour pressure over the range 293—322 K by effusion manometry. These results permit the determination of $\Delta H_f^\circ[P(CN)_3,g]$ and the mean P–CN bond dissociation energy.

EXPERIMENTAL

Materials.—Tricyanophosphine was prepared by the reaction of trichlorophosphine with silver cyanide according to Staats and Morgan.[3] The crude product was twice sublimed at 363 K and 0.01 Torr (Found: C, 32.8; N, 38.2; P, 28.2. Calc. for C_3N_3P: C, 33.0; N, 38.5; P, 28.4%). Titration of a hydrolysate against standard alkali using the first ionization of H_3PO_3 as end point indicated a purity of 99.0 mass-% (two determinations) for $P(CN)_3$.

Calorimeter.—This was the commercial LKB Precision Calorimetry System 8700–1 operated at 298.15 K and with the out-of-balance bridge signal displayed on a chart recorder. The calorimeter was tested by measuring the enthalpy of neutralisation of tris[(hydroxymethyl)amino]-methane (tham) in an excess of 0.1 mol dm^{-3} HCl for which $\Delta H(298.15\ \text{K},\ 1\,280 < n < 1\,464) = -7.104 \pm 0.006$ kcal mol^{-1}. Prosen and Kilday [4] obtained $\Delta H(298.15\ \text{K},\ n = 1\,345) = -7.115 \pm 0.007$ kcal mol^{-1} for the same reaction; n is the mole ratio of water to tham. Uncertainties are expressed as $\pm 2\bar{s}$, $\bar{s}$ being the standard deviation of the mean.

Effusion Manometer.—This manometer and its operation have been described previously.[5] The method involved weighing a Knudsen cell after known time intervals and relating the rate of weight loss to the equilibrium vapour

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† Throughout this paper, 1 cal = 4.184 J; 1 Torr = (101.325/760) kPa; 1 Å = 10^{-10} m.

[1] D. D. Wagman, W. H. Evans, V. B. Parker, J. Halow, S. M. Bailey, and R. H. Schumm, Nat. Bur. Stand. Tech. Note 270–3, U.S. Govt. Printing Office, Washington, D.C., 1968.

[2] CATCH tables, Phosphorus Compounds (A. J. Head), 1972, published by J. B. Pedley, School of Molecular Sciences, University of Sussex.

[3] P. A. Staats and H. W. Morgan, *Inorg. Synth.*, 1960, **6**, 84.

[4] E. J. Prosen and M. V. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, **A77**, 581.

[5] A. Finch, P. J. Gardner, and A. Hameed, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2869.

pressure. The test experiment with ferrocene was repeated successfully. In view of the ready hydrolysis of $P(CN)_3$ all loading and weighing operations were carried out in a dry nitrogen atmosphere. The calculation of vapour pressure from rate of weight loss requires an estimate of the collision diameter of $P(CN)_3(g)$. The crystallographic data of Emerson and Britton[6] were used to obtain this estimate except that the mean $N\hat{C}P$ was taken as 180° rather than 172° found crystallographically, it being assumed the contraction was due to crystal packing forces that are inoperative in the gas phase. Two methods of estimation were used; the first to determine the radius of the smallest circumscribing molecular sphere plus two van der Waals radii for nitrogen. The second method was to determine the diameter of the circumscribing sphere whose centre was at the centre of mass of $P(CN)_3$ (again corrected by adding two van der Waals radii for N). These estimates were 8.01 and 8.29 Å respectively. The sensitivity of the derived vapour pressures and enthalpy of sublimation to the choice of collision diameter was also investigated. For reasons mentioned previously[5] the slope (and hence the enthalpy of sublimation) of the $\log_{10}p$ *vs.* T^{-1} graph is more reliable than the absolute vapour pressures.

Reaction Stoicheiometry.—By use of a chromatographic method, Pollard *et al.*[7] report that the hydrolysis of $P(CN)_3$ in acid solution yields H_3PO_3 quantitatively. The calorimetric hydrolyses were performed in 100 cm^3 (or 25 cm^3) aliquots of deoxygenated distilled water which was presaturated at ambient temperature with HCN(g) prepared according to Mettee.[8] Hence the HCN is liberated in its standard state and the reaction examined is given by equation (1).

$$P(CN)_3(c) + (n + 3)H_2O(l) \longrightarrow H_3PO_3{\cdot}nH_2O(l) + 3HCN(g) \quad (1)$$

RESULTS

The enthalpies of hydrolysis for the reaction given by equation (1) are collected in Table 1.

TABLE 1

Reactant masses and enthalpy changes for reaction (1) at 298.15 K

m*/g	n	$-\Delta H_1$/kcal mol^{-1}
0.017 99	33 640	44.14
0.026 49	22 840	44.33
0.013 23	19 380	44.57
0.013 30	19 330	44.40
0.033 88	17 860	44.47
0.008 73 †	17 730	44.36
0.009 05 †	16 720	44.49
0.010 65 †	14 200	44.36
0.049 13	12 320	44.75
0.060 38	10 020	44.39
	$\langle -\Delta H_1 \rangle$ =	44.43 ($\bar{s}$ = 0.05)

* Sample mass *in vacuo*, corrected using density[6] for tricyanophosphine of 1.35 g cm^{-3}. † In a 25 cm^3 reaction vessel.

All results were corrected for the thermal effect of HCN(g) being evolved from the calorimetric liquid. The evolved gas was assumed to become saturated with water vapour and the thermal effect, calculated from the volume of the gas, the vapour pressure, and enthalpy of vaporization of water at 298.15 K, was approximately 2% of the total heat evolved. The mean value for ΔH_1 was corrected for the presence of 1.0 weight-% impurity, assumed inert (see Experimental section). Hence $\langle -\Delta H_1$, corrected$\rangle$ = 44.9 ± 0.1 kcal mol^{-1} from which $\Delta H_f°[P(CN)_3,c]$ = 117.9 ± 6.0 kcal mol^{-1} using equation (2). The following

$$\Delta H_f°[P(CN)_3,c] = 3\Delta H_f°[HCN,g] + \Delta H_f°[H_3PO_3{\cdot}nH_2O] - 3\Delta H_f°[H_2O,l] - \Delta H_1 \quad (2)$$

ancillary data at 298.15 K were used: $\Delta H_f°[HCN,g]$ = 32.3 ± 2.0,[9] $\Delta H_f°[H_3PO_3{\cdot}nH_2O]$ = −228.86 ± 0.53,[10] and $\Delta H_f°[H_2O,l]$ = −68.315 ± 0.010[11] kcal mol^{-1}. The large uncertainty in $\Delta H_f°[P(CN)_3,c]$ derives mainly from the uncertainty in $\Delta H_f°[HCN,g]$ and in the absence of this uncertainty is ±0.6 kcal mol^{-1}.

TABLE 2

Vapour pressure (p) and rate of weight loss ($\dot{w}$) of $P(CN)_3(c)$ as a function of temperature (T) calculated using σ = 8.01 Å and σ = 8.29 Å. (Effusion orifice radius = 1.849 × 10^{-4} m; effusion orifice length = 2.670 × 10^{-5} m)

T/K	$10^{11}\dot{w}$/kg s^{-1}	$10^3p(\sigma = 8.01$ Å$)$/ Torr	$10^3p(\sigma = 8.29$ Å$)$/ Torr
293.20	3.3345	0.917	0.916
295.65	3.9673	1.094	1.094
298.25	5.8500	1.617	1.617
300.05	7.5265	2.083	2.082
300.70	6.1911	1.718	1.717
303.05	6.8837	1.916	1.915
303.15	9.0227	2.506	2.504
303.70	8.2778	2.303	2.302
305.20	9.4601	2.636	2.633
306.55	11.047	3.079	3.076
308.25	15.760	4.383	4.378
308.30	14.152	3.943	3.938
310.35	17.437	4.857	4.851
311.75	15.546	4.349	4.344
311.95	16.826	4.703	4.696
313.20	23.003	6.401	6.390
313.65	25.831	7.172	7.158
315.60	28.361	7.879	7.863
318.23	32.755	9.098	9.077
320.80	61.054	16.58	16.51
322.85	48.324	13.32	13.28

TABLE 3

Bond energies (E), bond lengths (r), electronegativities (x) for $P(CN)_3$, and the phosphorus halides

	$\Delta H_f°[PX_3, g]$/ kcal mol^{-1}	E[a]/kcal mol^{-1}	r[b]/Å	x[c]
PF_3	−228.8 ± 0.3[d]	120	1.54	3.98
$P(CN)_3$	135.9 ± 6.0	84	1.78	3.3[e]
PCl_3	−68.6[1]	77	2.03	3.16
PBr_3	−33.3[1]	63	2.2	2.96
PI_3	1.3 ± 0.9[5]	50	2.5	2.66

[a] Ancillary data for this calculation were the standard heats of formation of gaseous F, CN, Cl, Br, I, and P taken as 18.88[1], 104.0[9], 29.08[1], 26.74[1], 25.53_5[1], and 75.20[1] kcal mol^{-1} respectively. [b] from Tables of Interatomic Distances and Configuration of Molecules and Ions, *Chem. Soc. Special Publ.* No. 11, 1958. [c] Pauling Scale from J. E. Huheey, ' Inorganic Chemistry,' Harper and Row, 1972. [d] G. K. Johnson, J. G. Melon, and W. N. Hubbard, *J. Chem. Thermodynamics*, 1972, **4**, 879. [e] Group electronegativity from Table 4.11 p. 167 in reference in footnote *c*.

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[6] K. Emerson and D. Britton, *Acta Cryst.*, 1964, **17**, 1134.

[7] F. H. Pollard, G. Nickless and M. T. Rothwell, *J. Chromatography*, 1963, **11**, 383.

[8] H. D. Mettee, *J. Phys. Chem.*, 1973, **77**, 1762.

[9] JANAF Thermochemical Tables, D. R. Stull and H. Prophet, Nat. Bur. Stand., U.S. Govt. Printing Office, Washington, D.C., 1971.

[10] A. Finch, P. J. Gardner, and C. P. McDermott, *J. Chem. Thermodynamics*, 1974, **6**, 259.

[11] CODATA Recommended Key Values for Thermodynamics, *J. Chem. Thermodynamics*, 1975, **7**, 1.

The vapour pressures obtained from the effusion manometric experiments and calculated using the two possible choices of collision diameter (σ) (see Experimental section) are collected in Table 2.

The sensitivity of vapour pressure and standard enthalpy of sublimation to choice of collision diameter (over the range 4.0 to 12.0 Å) was calculated at 298.15 K as -0.0026 Torr Å^{-1} and -0.07 kcal mol^{-1} Å^{-1} respectively. The vapour pressure equation for $\sigma = 8.29$ Å was

$$\ln(p/\text{Torr}) = -(9\,041.0 \pm 342.7)/T + (23.775 \pm 1.114)$$

where the uncertainties[12] are $\pm[\Sigma\delta^2/(n-2)(\Sigma x^2 - n\langle x\rangle^2)]^{\frac{1}{2}}$ and $\pm[\Sigma\delta^2\Sigma x^2/n(n-2)(\Sigma x^2 - n\langle x\rangle^2)]^{\frac{1}{2}}$ respectively where δ = residual in $\log_e p$, $x = T^{-1}$, and n is the number of sets.

DISCUSSION

Mean bond energies [calculated from equation (3)] for $P(CN)_3$ and the phosphorus halides are compared in Table 3 with electronegativities, and bond lengths

$$\bar{D}(\text{P–X}) = 1/3(3\Delta H_f^\circ[\text{X,g}] + \Delta H_f^\circ[\text{P,g}] - \Delta H_f^\circ[\text{PX}_3\text{,g}]) \quad (3)$$

From the data collected in Table 3 it is evident that there is a smooth correlation between $\bar{D}$(P–X) and bond length or electronegativity with CN falling between F and Cl in the series.

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[12] P. D. Lark, B. R. Craven, and R. C. L. Bosworth, 'The Handling of Chemical Data,' Pergamon Press, London, 1969.