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The enthalpies of formation of bis(dimethylamino)cyanophosphine, (dimethylamino)dicyanophosphine, and tricyanophosphine

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The standard molar enthalpies of formation at the temperature 298.15 K of $\{(CH_3)_2N\}_2PCN(l)$, $(CH_3)_2NP(CN)_2(l)$, and $P(CN)_3(cr)$ have been determined by reaction calorimetry as $-(0.4 \pm 3.2)\ kJ\cdot mol^{-1}$, $(189.3 \pm 5.0)\ kJ\cdot mol^{-1}$, and $(373.1 \pm 6.8)\ kJ\cdot mol^{-1}$, respectively. Enthalpies of vaporization have been obtained from vapour-pressure measurements for the first two compounds and the corresponding values of $\Delta_f H^\circ_m(g)/(kJ\cdot mol^{-1})$ derived as (54.2 ± 3.5), (228.7 ± 5.5), and (448.4 ± 7.4), respectively. The values of the bond enthalpies D(P–CN) in the cyanophosphines are discussed.

1. Introduction

This paper reports thermochemical measurements by solution-reaction calorimetry leading to the molar enthalpies of formation of $\{(CH_3)_2N\}_vP(CN)_{3-v}$, (where $v = 0, 1, 2$) in the condensed state. Values for the compounds where $v = 1, 2$ have not been reported previously and the new value for $P(CN)_3$ disagrees with the current literature value; the discrepancy is discussed and resolved. Enthalpies of vaporization at the temperature $T = 298.15$ K for two compounds ($v = 1, 2$) have been derived from vapour-pressure measurements. This study provides further information on the enthalpies of (P–CN) bonds and extends the work previously reported on the thermochemistry of (dimethylamino)chlorophosphines.(1)

2. Experimental

Bis(dimethylamino)cyanophosphine was prepared by refluxing a stirred stoichiometric mixture of $\{(CH_3)_2N\}_2PCl(l)$, prepared as described in reference 1, and AgCN in trichloromethane for 12 h. The product was filtered from AgCl, the

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solvent removed by pumping, and the residue distilled under reduced pressure. The liquid boiling at temperatures between 325 K and 326 K (pressure $p = 0.20$ kPa) was collected and allowed to solidify (melting temperature: 294 K to 296 K) in the condenser. The purity was estimated, after hydrolysis with excess HCl and subsequent oxidation with H_2O_2 of the H_3PO_3 produced, by titrimetric determination (standard NaOH) of the H_3PO_4. The difference between the two end-points yields a value for the mole fraction of P: found, 0.2130; calculated for $C_5H_{12}N_3P$, 0.2134.

(Dimethylamino)dicyanophosphine was prepared by refluxing a stoichiometric mixture of $(CH_3)_2NPCl_2$(l), prepared as described in reference 1, and AgCN in acetonitrile for 20 h with stirring. The mixture was filtered under nitrogen, the solvent removed by pumping, and the product distilled under reduced pressure followed by two further distillations (boiling temperature: 339 K to 341 K at $p = 0.13$ kPa). The purity was assessed by determination of the mole fraction of P by the method described above: found, 0.2420; calculated for $C_4H_6N_3P$, 0.2437.

Tricyanophosphine was prepared according to the method described by Jones and Coskran.(2) A mixture of dry AgCN and freshly-distilled PCl_3 was stirred in acetonitrile (dried over CaH_2) for 3 h under nitrogen at room temperature. The mixture was filtered to remove AgCl, the solvent removed, and the crude product twice sublimed *in vacuo*. The mass-fraction purity was assessed as 0.995 by the method described for the other cyanophosphines.

Enthalpies of hydrolysis of the three compounds were determined using an isoperibol twin-vessel solution-reaction calorimeter.(3) The calorimeter was operated at $T = 298.15$ K and the precision and accuracy of the results were frequently successfully checked by measurements of the molar enthalpy of neutralization of tris(hydroxymethyl)aminomethane (THAM) with excess $0.1\ \mathrm{mol \cdot dm^{-3}}$ HCl(aq).

Bis(dimethylamino)cyanophosphine and (dimethylamino)dicyanophosphine both undergo rapid hydrolysis in water and HCl(aq). To avoid the formation of an unidentified yellow precipitate which formed when the latter compound reacted with water alone, $2\ \mathrm{mol \cdot dm^{-3}}$ HCl(aq) was used in the calorimetric experiments on both compounds.

The hydrolysis of $P(CN)_3$ in $2\ \mathrm{mol \cdot dm^{-3}}$ HCl(aq) has been reported to yield H_3PO_3 as the only phosphorus-containing product, whereas the reaction with $5\ \mathrm{mol \cdot dm^{-3}}$ NaOH(aq) resulted in approximately 20 per cent of the phosphorus as species other than HPO_3^{2-}.(4) The formation of by-products, however, appears to be related to the violence of the reaction since the aqueous alkaline hydrolysis of a solution of $P(CN)_3$ in diethyl ether produced only HPO_3^{2-}. In the present study the hydrolysis of $P(CN)_3$ was investigated using (i), de-ionised de-oxygenated water; (ii), water containing dissolved HCN; and (iii), $0.5\ \mathrm{mol \cdot dm^{-3}}$ NaOH(aq) where, after hydrolysis, Na_2HPO_3 was assumed to be the only phosphorus-containing product. Titration of the alkaline hydrolysate with standard HCl(aq) produced the calculated difference between the first (Na_2HPO_3) and second (NaH_2PO_3) end-points, and between the second and third (NaCN) end-points for the reaction:

$$P(CN)_3 + 5NaOH = Na_2HPO_3 + 3NaCN + 2H_2O.$$

TABLE 1. Hydrolysis of a mass m of $\{(CH_3)_2N\}_2PCN(l)$ in a volume 100 cm^3 of 2 $mol \cdot dm^{-3}$ HCl(aq) $\hat{=}$ (HCl in $27.76H_2O$) at $T = 298.15$ K {equation (1)}

m/g [a]	$-\Delta_r H_m/(kJ \cdot mol^{-1})$ (observed)	$\Delta H_m/(kJ \cdot mol^{-1})$ (concentration)	$-\Delta_r H_m/(kJ \cdot mol^{-1})$ (corrected)
0.01707	240.34	3.60	236.74
0.01878	241.30	3.47	237.83
0.02725	241.38	3.52	237.86
0.03132	241.29	3.49	237.80
0.03259	241.44	3.47	237.97
0.04066	240.55	3.49	237.06
0.05427	241.53	3.50	238.03
		Mean:	237.61 (±0.46)

[a] Weighings in air corrected using $\rho/(g \cdot cm^{-3}) = 0.974$,(15) where ρ denotes density.

With all three hydrolytic agents the reaction was shown to be complete within the main reaction period (about 10 min) of a calorimetric experiment.

Vapour pressures were determined using the apparatus previously described.(1)

3. Results

The results obtained for the hydrolysis of $\{(CH_3)_2N\}_2PCN$ and $(CH_3)_2NP(CN)_2$ are reported in tables 1 and 2, respectively, and refer to the reactions:

$$\{(CH_3)_2N\}_2PCN(l) + \{(m+2)HCl + (p+3)H_2O\}(sln) = \{2(CH_3)_2NH_2Cl + H_3PO_3 + mHCl + pH_2O + HCN\}(sln), \quad (1)$$

$$(CH_3)_2NP(CN)_2 + \{(m+1)HCl + (p+3)H_2O\}(sln) = \{(CH_3)_2NH_2Cl + H_3PO_3 + mHCl + pH_2O + 2HCN\}(sln). \quad (2)$$

Because the reactions involve consumption of HCl, the results include a correction term for concentration of the final solution to the initial composition of (HCl + $27.76H_2O$). The molar enthalpies of solution of H_3PO_3(cr) and $(CH_3)_2NH_2Cl$(cr)

TABLE 2. Hydrolysis of a mass m of $(CH_3)_2NP(CN)_2(l)$ in a volume 100 cm^3 of 2 $mol \cdot dm^{-3}$ HCl(aq) $\hat{=}$ (HCl in $27.76H_2O$) at $T = 298.15$ K {equation (2)}

m/g [a]	$-\Delta_r H_m/(kJ \cdot mol^{-1})$ (observed)	$\Delta H_m/(kJ \cdot mol^{-1})$ (concentration)	$-\Delta_r H_m/(kJ \cdot mol^{-1})$ (corrected)
0.01281	210.79	1.58	209.21
0.02286	210.72	1.62	209.10
0.02292	210.00	1.61	208.39
0.02814	211.86	1.61	210.25
0.03076	210.99	1.64	209.35
0.04127	210.76	1.67	209.09
0.04512	210.00	1.64	208.36
		Mean:	209.11 (±0.59)

[a] Weighings in air corrected using $\rho/(g \cdot cm^{-3}) = 1.077$.(15)

TABLE 3. Hydrolysis of a mass m of $P(CN)_3$(cr) at $T = 298.15$ K in a volume 100 cm^3 of (a), de-oxygenated de-ionised water; and (b), de-oxygenated de-ionised water containing HCN (concentration about 0.01 $mol \cdot dm^{-3}$)

	$\frac{m}{g}$ [a]	$\frac{-\Delta_r H_m}{kJ \cdot mol^{-1}}$	$\frac{-\Delta_{sol} H_m(H_3PO_3)}{kJ \cdot mol^{-1}}$	$\frac{\Delta_f H^\circ_m\{P(CN)_3, cr\}}{kJ \cdot mol^{-1}}$
(a)	0.01583	186.65	5.59	371.55
	0.02770	185.41	5.34	370.56
	0.03411	188.21	5.23	373.47
	0.03992	184.76	5.14	370.11
	0.04102	184.44	5.12	369.81
	0.04116	184.33	5.12	369.70
	0.04270	185.80	5.10	371.19
	0.05845	186.02	4.89	371.62
			Mean:	371.00 (±1.04)
(b)	0.09585	184.01	4.47	370.03
	0.09597	184.68	4.47	370.70
	0.10302	185.27	4.41	371.35
			Mean:	370.69

[a] Weighings in air corrected using $\rho = 1.35\ g \cdot cm^{-3}$.(16)

in (HCl + $27.76H_2O$) have been reported as (7.94 ± 0.17) $kJ \cdot mol^{-1}$ and (3.24 ± 0.01) $kJ \cdot mol^{-1}$, respectively, and showed no concentration dependence over the ranges studied.(1) Thus, using the following ancillary values of $\Delta_f H^\circ_m/(kJ \cdot mol^{-1})$: (HCl in $27.76H_2O$), $-(164.44 \pm 0.10)$;(1) H_3PO_3(cr), $-(957.1 \pm 2.3)$;(1) $(CH_3)_2NH_2Cl$(cr), $-(289.21 \pm 0.03)$;(1) H_2O(l), $-(285.83 \pm 0.04)$;(5) and HCN(aq), (96.7 ± 2.2):

$$\Delta_f H^\circ_m[\{(CH_3)_2N\}_2PCN] = -(0.4 \pm 3.2)\ kJ \cdot mol^{-1},$$

neglecting any enthalpy of mixing between $(CH_3)_2NH_2Cl$ and H_3PO_3 in HCl solution.† The value for $\Delta_f H^\circ_m$(HCN, aq) was derived from $\Delta_f H^\circ_m(CN^-, aq)/(kJ \cdot mol^{-1}) = (140.3 \pm 2.2)$,(6) and the molar enthalpy of ionization of HCN(aq):(7) (43.6 ± 0.1) $kJ \cdot mol^{-1}$. Similarly, using the same ancillary quantities:

$$\Delta_f H^\circ_m\{(CH_3)_2NP(CN)_2\} = (189.3 \pm 5.0)\ kJ \cdot mol^{-1}.$$

The results obtained for the hydrolysis of $P(CN)_3$(cr) using (a), de-oxygenated deionised water; and (b), water containing dissolved HCN(g), are reported in table 3. Davies *et al.*(8) carried out a similar determination at $T = 298.15$ K using distilled water "pre-saturated at ambient temperature" with HCN(g), assuming that the HCN (boiling temperature: 299 K) produced would be wholly gaseous under these conditions. HCN is, however, infinitely soluble in water and the reaction product must, therefore, be HCN(aq). The results listed in table 3 confirm that there is no significant difference between the values obtained using water and HCN(aq) as hydrolytic reagents. The physical state of the HCN produced in this reaction was further confirmed by measuring the molar enthalpy of reaction between NaCN(cr)

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† Throughout this paper uncertainty intervals of reported experimental results denote 95 per cent confidence limits, calculated using Student's *t* at the appropriate number of degrees of freedom.

TABLE 4. Hydrolysis of a mass m of $P(CN)_3(cr)$ in a volume $100\ cm^3$ of $0.5\ mol\cdot dm^{-3}$ NaOH(aq) at $T = 298.15$ K {equation (3)}

m/g	$n(H_2O)/n\{P(CN_3)\}$	$-\Delta_r H_m/(kJ\cdot mol^{-1})$
0.04114	14710	343.97
0.04982	12140	343.97
0.05267	11490	343.26
0.05534	10930	343.59
0.06217	9732	344.72
0.06891	8780	345.01
0.07159	8452	344.05
0.07789	7768	343.97
0.08653	6992	344.09
0.12938	4677	344.72
	Mean:	344.14 ± 0.38

and $0.1\ mol\cdot dm^{-3}$ HCl(aq) at (293.65, 298.15, and 303.15) K. The results were independent of temperature, indicating that HCN(g) was not a reaction product, even at 4 K above the boiling temperature of HCN(l). The presence of H_3PO_3 ($pK_a = 2.0$) in the solution {about (1.5 to 5.4) $mmol\cdot dm^{-3}$} was sufficient to suppress completely the ionisation of the very weak hydrocyanic acid ($pK_a = 9.3$).

The value of $\Delta_f H_m^\circ(H_3PO_3, aq)$ has been derived from that for $H_3PO_3(cr)$ (see above) and recent measurements of $\Delta_{sol} H_m(H_3PO_3, cr)$, which show a marked concentration dependence.(9) The appropriate molar enthalpy of solution, calculated from equation (2) in reference 9, is included in table 3. Thus from the reaction:

$$P(CN)_3(cr) + 3H_2O(l) = H_3PO_3(aq) + 3HCN(aq,\ undissociated),$$

using the auxiliary thermodynamic quantities given above,

$$\Delta_f H_m^\circ\{P(CN_3), cr\} = (371.0 \pm 7.1)\ kJ\cdot mol^{-1}.$$

The results for the alkaline hydrolysis of $P(CN)_3$ are reported in table 4 and refer to the reaction:

$$P(CN)_3(cr) + \{(m+5)NaOH + (p-2)H_2O\}(sln) = \\ \{Na_2HPO_3 + 3NaCN + mNaOH + pH_2O\}(sln), \quad (3)$$

where $\{(p-2)/(m+5)\} = 111$.

The molar enthalpy of neutralization of $H_3PO_3(cr)$ with $0.5\ mol\cdot dm^{-3}$ NaOH(aq) was also measured and the results are reported in table 5 and refer to the reaction:

$$H_3PO_3(cr) + \{(m+5)NaOH + (p-2)H_2O\}(sln) = \\ \{Na_2HPO_3 + (m+3)NaOH + pH_2O\}(sln). \quad (4)$$

These measurements were also carried out in the presence of NaCN {mole ratio $n(NaCN)/n(H_3PO_3) = 3.0$} which had no significant effect on the results previously obtained (table 5).

TABLE 5. Neutralization of a mass m of H_3PO_3(cr) at $T = 298.15$ K with a volume 100 $\mathrm{cm^3}$ of (a), 0.5 $\mathrm{mol \cdot dm^{-3}}$ NaOH(aq) {equation (4)}; and (b), 0.5 $\mathrm{mol \cdot dm^{-3}}$ NaOH(a) containing NaCN $\{n(\mathrm{NaCN})/n(\mathrm{H_3PO_3}) = 3.0\}$

	m/g [a]	$n(\mathrm{H_2O})/n(\mathrm{H_3PO_3})$	$-\Delta_r H_m/(\mathrm{kJ \cdot mol^{-1}})$
(a)	0.04624	9844	122.67
	0.05906	7707	121.50
	0.07587	5999	121.46
	0.07637	5960	122.51
	0.08914	5706	122.38
	0.11205	4062	122.88
		Mean:	122.23 ± 0.64
(b)	0.06035	7542	121.96
	0.08616	5283	123.18
	0.09113	4995	121.50
	0.12584	3617	123.22
		Mean:	122.47 ± 1.38

[a] Weighings in air corrected using $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.651$.(17)

The molar enthalpy of the reaction:

$$\mathrm{P(CN)_3(cr) + 3NaOH(cr) = 3NaCN(aq) + H_3PO_3(cr)}, \qquad (5)$$

may be obtained from $\Delta H_m(5) = \Delta H_m(3) - \Delta H_m(4) - \Delta H_m(6) = -(354.18 \pm 0.77)\ \mathrm{kJ \cdot mol^{-1}}$, where $\Delta H_m(6)$ is calculated from literature values(10) of $\Delta_f H_m^\circ$ for the components of the reaction:

$$\{\mathrm{Na_2HPO_3} + (m+3)\mathrm{NaOH} + p\mathrm{H_2O}\}(\mathrm{sln}) = \\ 3\mathrm{NaOH(cr)} + (\mathrm{Na_2HPO_3} + m\mathrm{NaOH} + p\mathrm{H_2O})(\mathrm{sln}). \qquad (6)$$

This calculation was made by re-arranging the relation derived from equation (6) in the form:

$$\begin{aligned}\Delta H_m(6) &= 3\cdot\Delta_f H_m^\circ(\mathrm{NaOH, cr}) + \Delta_f H_m^\circ(m\mathrm{NaOH\ in\ }p\mathrm{H_2O, sln}) - \\ &\quad \Delta_f H_m^\circ\{(m+3)\mathrm{NaOH\ in\ }p\mathrm{H_2O, sln}\} \\ &= 3\cdot\Delta_f H_m^\circ(\mathrm{NaOH, cr}) - \\ &\quad 3\cdot\Delta_f H_m^\circ[\mathrm{NaOH\ in\ }\{p/(m+3)\}\mathrm{H_2O, sln}] + \\ &\quad m\cdot\Delta_f H_m^\circ\{\mathrm{NaOH\ in\ }(p/m)\mathrm{H_2O, sln}\} - \\ &\quad m\cdot\Delta_f H_m^\circ[\mathrm{NaOH\ in\ }\{p/(m+3)\}\mathrm{H_2O, sln}].\end{aligned}$$

Substituting values obtained from reference 10, with $m = 45$ and $p = 5553$,

$$\Delta H_m(5) = (132.3 \pm 0.2)\ \mathrm{kJ \cdot mol^{-1}}, \quad \text{(estimated uncertainty)}.$$

The value: $\Delta_f H_m^\circ/(\mathrm{kJ \cdot mol^{-1}}) = -425.86$ for NaOH(cr) was derived from the value in reference 10, corrected for the difference between the values for NaOH(aq,∞) in reference 10 and the more recent reference 5. The value: $\Delta_f H_m^\circ/(\mathrm{kJ \cdot mol^{-1}}) = -(100.2 \pm 2.2)$ for NaCN(aq,∞) was obtained from the values for $\mathrm{Na^+}$(aq,∞),(5)

TABLE 6. $\Delta_f H^\circ_m$(l or cr), $\Delta_{vap} H^\circ_m$(l or cr), and $\Delta_f H^\circ_m$(g) for $\{(CH_3)_2N\}_v P(CN)_{3-v}$ ($v = 0, 1, 2$) at $T = 298.15$ K

	$\frac{\Delta_f H^\circ_m(\text{l or cr})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{vap} H^\circ_m(\text{l or cr})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_f H^\circ_m(\text{g})}{\text{kJ}\cdot\text{mol}^{-1}}$
0	373.1 ± 6.8	75.3 ± 2.9	448.4 ± 7.4
1	189.3 ± 5.0	39.4 ± 2.3	228.7 ± 5.5
2	-0.4 ± 3.2	54.6 ± 1.4	54.2 ± 3.5

and CN^-(aq,∞);[6] no correction was applied for concentration to the final state of reaction (3): NaCN in $1850H_2O$. Using these values for $\Delta_f H^\circ_m$ of NaOH(cr) and NaCN(aq), and those previously listed for $\Delta_f H^\circ_m(H_3PO_3,\text{cr})$ and $\Delta H_m(5)$:

$$\Delta_f H^\circ_m\{P(CN)_3,\text{cr}\} = (374.7 \pm 7.0)\ \text{kJ}\cdot\text{mol}^{-1}.$$

The difference between the two values obtained for $\Delta_f H^\circ_m\{P(CN)_3,\text{cr}\}$ is $(3.7 \pm 3.5)\ \text{kJ}\cdot\text{mol}^{-1}$, ignoring the uncertainty associated with $\Delta_f H^\circ_m(\text{CN},\infty)$, which is common to both determinations. A simple statistical test (t test) reveals that this difference is not significant and we recommend the weighted mean value:

$$\Delta_f H^\circ_m\{P(CN)_3,\text{cr}\} = (373.1 \pm 6.8)\ \text{kJ}\cdot\text{mol}^{-1}.$$

Molar enthalpies of vaporization for $\{(CH_3)_2N\}_v P(CN)_{3-v}$ ($v = 1, 2$) were derived from vapour-pressure measurements over temperature ranges which included 298.15 K and are reported in table 6, together with the corresponding values of $\Delta_f H^\circ_m(\text{g})$. The value $\Delta_{sub} H^\circ_m\{P(CN)_3,\text{cr}\} = (75.3 \pm 2.9)\ \text{kJ}\cdot\text{mol}^{-1}$, obtained by effusion manometry, was taken from reference 8.

4. Discussion

No values of $\Delta_f H^\circ_m$(l) or $\Delta_f H^\circ_m$(g) for $(CH_3)_2NP(CN)_2$ or $\{(CH_3)_2\}_2PCN$ have been previously reported. The two values obtained for $\Delta_f H^\circ_m\{P(CN_3),\text{cr}\}$ obtained by neutral and alkaline hydrolysis are in good agreement: most of the uncertainty of $\pm 7\ \text{kJ}\cdot\text{mol}^{-1}$ arises because of the uncertainty in $\Delta_f H^\circ_m(CN^-,\text{aq})$, which is common to both determinations. The experimental results for neutral hydrolysis reported herein and by Davies *et al.*[8] are in excellent agreement. However, misinterpretation of their measurements by the latter authors and the use of an early value for $\Delta_f H^\circ_m(\text{HCN},\text{g})$ led to an erroneous value for $\Delta_f H^\circ_m\{P(CN)_3,\text{cr}\}$: $\{(493 \pm 25)\ \text{kJ}\cdot\text{mol}^{-1}\}$.

An estimate of $\Delta_f H^\circ_m\{P(CN)_3,\text{g}\}$ has been made by *ab initio* molecular-orbital calculation[11] of the molar electronic-energy change at $T \rightarrow 0$ for the isogyric (spin-conserved) reaction:

$$PH_3(\text{g}) + 3HCN(\text{g}) = P(CN)_3(\text{g}) + 3H_2(\text{g}). \qquad (7)$$

After correcting this molar energy change for changes in zero-temperature molar energy and for the change in molar enthalpy increment: $\Delta\Delta_0^{298.15\,\text{K}} H^\circ_m(7)$, $\Delta_r H_m(7, 298.15\ \text{K}) = (82.4 \pm 13)\ \text{kJ}\cdot\text{mol}^{-1}$, from which $\Delta_f H^\circ_m\{P(CN)_3,\text{g}\} =$

$(459 \pm 15)\ \mathrm{kJ\cdot mol^{-1}}$, using $\Delta_f H_m^\circ(298.15\ \mathrm{K})/(\mathrm{kJ\cdot mol^{-1}}) = (5.4 \pm 1.7)$, and (123.7 ± 2.2), for $PH_3(g)$,(12) and HCN(g),(6) respectively. An earlier report(11) using the same method gave $\Delta_f H_m^\circ\{P(CN)_3,g\} = (493 \pm 15)\ \mathrm{kJ\cdot mol^{-1}}$, but this was calculated using $\Delta_f H_m^\circ(HCN,g) = 135.1\ \mathrm{kJ\cdot mol^{-1}}$,(10) a value to which some doubt has been ascribed.(6) The new calculated value: $\Delta_f H_m^\circ\{P(CN)_3,g\} = (459 \pm 15)\ \mathrm{kJ\cdot mol^{-1}}$ overlaps with the experimental result reported here: $(448 \pm 7)\ \mathrm{kJ\cdot mol^{-1}}$.

The enthalpy changes for the redistribution reactions:

$$(1/3)P(CN)_3(g) + (2/3)\{(CH_3)_2N\}_3P(g) = \{(CH_3)_2N\}_2P(CN)(g), \tag{8}$$

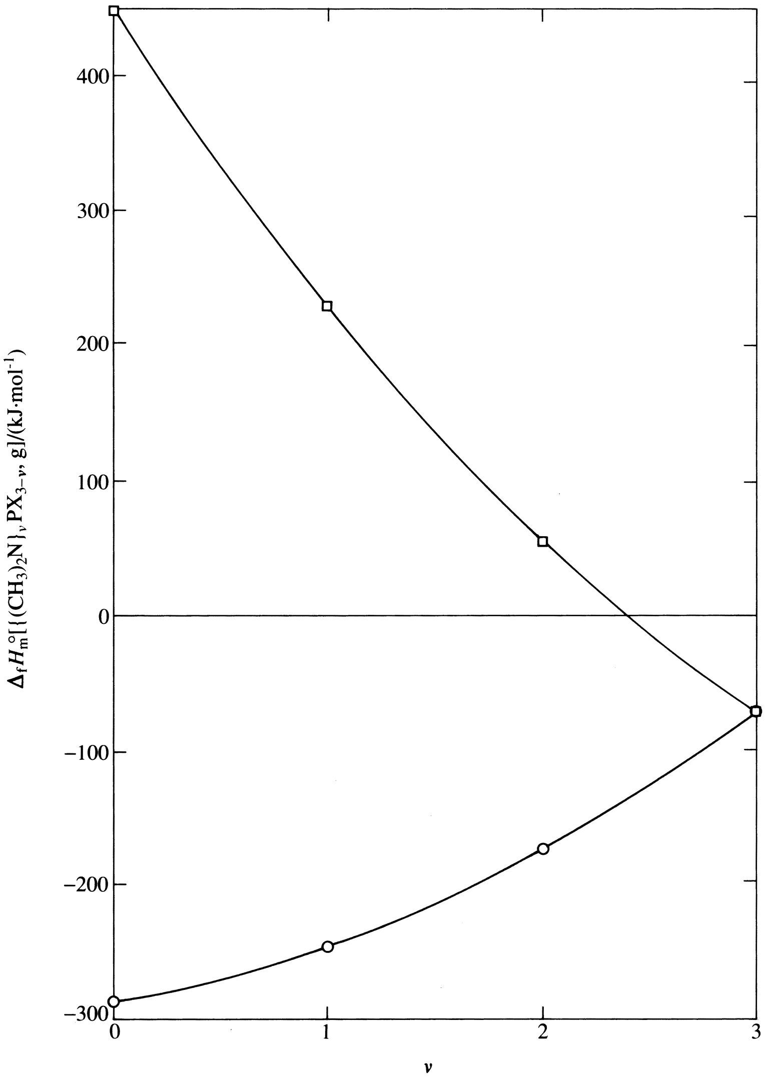

FIGURE 1. Effect on $\Delta_f H_m^\circ(g)$ of progressive substitution of $(CH_3)_2N$– in $\{(CH_3)_2N\}_3P$ by ○, Cl; □, CN.

$$(2/3)P(CN)_3(g) + (1/3)\{(CH_3)_2N\}_3P(g) = (CH_3)_2NP(CN)_2(g), \qquad (9)$$

$$\Delta_r H^\circ_m(8) = -(47.8 \pm 4.6)\ \mathrm{kJ \cdot mol^{-1}}; \quad \Delta_r H^\circ_m(9) = -(46.4 \pm 7.4)\ \mathrm{kJ \cdot mol^{-1}}.$$

provide a useful check on the internal consistency of the results. Comparison with the limited values available for P(III) compounds(13) suggests that these values are reasonable. It is interesting to note that these molar redistribution enthalpies are about 50 per cent larger than the corresponding values(1) for the (dimethylamino)-chlorophosphines; this is a consequence of the fact that $\langle D \rangle$(P–CN) (see below) is 73 kJ·mol^{-1} larger than $\langle D \rangle$(P–Cl).

The mean bond-dissociation enthalpy: $\langle D \rangle$(P–CN) = (394.7 ± 3.2) kJ·mol^{-1} is readily obtained from our experimental result, using $\Delta_f H^\circ_m$((P,g) = (316.5 ± 1.0) kJ·mol^{-1},(5) and $\Delta_f H^\circ_m$(CN,g) = (438.7 ± 2.0) kJ·mol^{-1}. The latter value is derived from a recent study(14) of the photodissociation of $(CN)_2$ from which $\Delta_f H^\circ_m(\mathrm{CN,g}, T \rightarrow 0)$ = (435.4 ± 2.0) kJ·mol^{-1}, corrected to $T = 298.15$ K using the value of $\Delta\Delta_0^{298.15\,\mathrm{K}} H^\circ_m$ from reference 10. Cyanide is a pseudohalogen and this result places $\langle D \rangle$(P–CN) between $\langle D \rangle$(P–F) (506 kJ·mol^{-1}) and $\langle D \rangle$(P–Cl) (322 kJ·mol^{-1}).

Assuming the transferability of $\langle D \rangle\{P\text{–}N(CH_3)_2\}$ in $\{(CH_3)_2N\}_3P$,(1) (274 ± 8) kJ·mol^{-1}, into the (dimethylamino)cyanophosphines, the following bond enthalpies have been calculated, using the auxiliary quantities listed above:

$$E(\mathrm{P–CN})\ \text{in}\ (CH_3)_2NP(CN)_2 = (418 \pm 7)\ \mathrm{kJ \cdot mol^{-1}},$$

$$E(\mathrm{P–CN})\ \text{in}\ \{(CH_3)_2N\}_2PCN = (443 \pm 20)\ \mathrm{kJ \cdot mol^{-1}}.$$

The effect of progressive substitution by CN on the molar enthalpy of formation of $\{(CH_3)_2N\}_3P(g)$ is shown in figure 1. The non-linearity of the curve demonstrates that the bond-dissociation enthalpies $\langle D \rangle$(P–N) and $\langle D \rangle$(P–CN) are not constant in the series, which is further shown by the fact that the enthalpies of the redistribution reactions are not zero (see above). The corresponding values for the chloro-substituted dimethylaminophosphines(1) are included in the figure which shows smooth curves for both series.

Despite the satisfactory agreement between these two solution-reaction calorimetric results for $\Delta_f H^\circ_m\{P(CN)_3,\mathrm{cr}\}$, they both depend on ancillary values of $\Delta_f H^\circ_m$ for H_3PO_3 and CN^-(aq). Two additional procedures are appropriate for independent further measurements, namely rotating-bomb calorimetry and fluorine-bomb calorimetry; this is discussed elsewhere.(18)

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