

## The standard enthalpies of formation of hydrogen cyanide and tricyanophosphine by ab initio molecular orbital calculation

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### Abstract

The standard enthalpies of formation of HCN(g) and P(CN)<sub>3</sub>(g) at 298.15 K were determined by ab initio molecular orbital calculation as  $137 \pm 10$  and  $493 \pm 15$  kJ mol<sup>-1</sup> respectively; these results are compared with the best available experimental results.

### INTRODUCTION

The standard enthalpy of formation of crystalline tricyanophosphine was reported in 1976 as  $493 \pm 25$  kJ mol<sup>-1</sup> from a reaction calorimetric study [1] at 25°C of the hydrolysis reaction to phosphorous acid H<sub>3</sub>PO<sub>3</sub> and hydrogen cyanide. The enthalpy of sublimation was derived [1] from an effusion manometric determination of the vapour pressures over the temperature range 293–333 K; combination of these enthalpies gave  $\Delta H_f^\circ[\text{P(CN)}_3, \text{g}]_{298.15} = 569 \pm 25$  kJ mol<sup>-1</sup>. Recently it has been suggested [2] that this result is ca. 200 kJ mol<sup>-1</sup> too high. The evidence was derived from an empirical correlation between  $\Delta H_f^\circ[\text{PX}_3, \text{g}]$  and  $\Delta H_f^\circ[\text{CX}_4, \text{g}]$ , where X is halogen or pseudohalogen. This has prompted a re-examination [3] of the calorimetry of the hydrolysis, and particular attention has been directed at the constitution of the final thermodynamic state (the hydrolysate) and the ancillary thermodynamic data used for the components of that state. The standard enthalpy of formation of H<sub>3</sub>PO<sub>3</sub>(c) is well-established [4] although a recent report [5] of its enthalpy of solution ( $-6.3 \pm 0.6$  kJ mol<sup>-1</sup>) differs from the value used in the original study ( $-0.1 \pm 0.1$  kJ mol<sup>-1</sup>) [1]. The standard enthalpy of formation of HCN(g) (this was the

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identified physical state in the 1976 paper [1]) is derived from results reported in the nineteenth century by Berthelot [6].

This paper describes the calculation by ab initio methods of the standard enthalpies of the formation of HCN(g) and P(CN)<sub>3</sub>(g) and compares these calculated results with the experimental results outlined above. A resolution of the controversy concerning  $\Delta H_f^\circ[\text{P(CN)}_3, \text{g}]$  is proposed.

Molecular orbital calculations are either semi-empirical, that is parameterized, or ab initio (or nonempirical) and contain no parameterization [7]. Semi-empirical routines will often produce quite reliable enthalpies of formation but, ultimately, the accuracy of such results depends on the quality of the parameterization; such routines will not be discussed further here.

Ab initio packages do not usually generate standard enthalpies of formation because of their inability to reproduce the electron correlation energy exactly [7,8]. The electronic energy is usually calculated via a self consistent field (SCF) approach, and the result obtained using the “best” choice of wave functions is known as the Hartree–Fock (HF) limit; the difference between the HF limit and the exact result is the electron correlation energy. Accurate calculation of the correlation energy is computationally very demanding, requiring roughly an order of magnitude more resource than that required for the calculation of the HF limit. Consequently most studies estimate the correlation energy using perturbation theory, usually that of Møller and Plesset [9] and abbreviated MP $n$ , where the integer  $n$  identifies the point of truncation in the perturbation equation.

The total energy including the estimated correlation energy is an electronic energy of a hypothetical gaseous and vibrationless molecular configuration at 0 K. Molar energy changes for chemical reactions may be calculated using these energies; in thermodynamic terms these are internal energy changes. These changes in internal energy may be corrected for changes in zero point energies and the enthalpy function ( $H_{298}^\circ - H_0^\circ$ ) to become enthalpy changes at 298.15 K. Such results may be compared with the corresponding results obtained from experimental data or a single value for  $\Delta H_f^\circ$  of one component extracted. This procedure has been applied on many occasions to compounds of the elements of the first short period [8,10], to homologous series, e.g. amines [11], and particularly to hydrides [12,13]. Single molecules, e.g. NH<sub>3</sub> [14], or radicals, e.g. HO<sub>2</sub> [15], have received detailed attention with increasingly sophisticated wave functions and correlational energy estimation procedures to illustrate the convergence of the computational procedures under these conditions. In the study of NH<sub>3</sub> [14], the “best” calculated  $\Delta H_f^\circ$  at 0 K was  $-36.8 \pm 2.1$  kJ mol<sup>-1</sup>, compared with the recommended value [16] of  $-38.91 \pm 0.35$  kJ mol<sup>-1</sup>. In general, the accuracy with which heats of formation of such species may be calculated [10] varies from  $\pm 4$  to  $\pm 10$  kJ mol<sup>-1</sup>; clearly the

most accurate calculated results are still an order of magnitude inferior in accuracy to the best experimental results. However, for many species that are unstable ( $\cdot\text{HO}_2$ ) or difficult to handle ( $\text{PH}_3$ ), calculational methods will yield  $\Delta H_f^\circ$  that are comparable with those obtained from the most sophisticated experimental thermochemistry.

For compounds of the second row elements (and heavier), the situation is more uncertain [8]; the accuracy of computational methods is correspondingly lower and extensive use is made of spin-conserved (see Results section) reactions [8] to predict  $\Delta H_f^\circ$ . For example, a recent study [17] to calculate the  $\Delta H_f^\circ$  of the methyl substituted disilanes yielded agreement with experimental values to  $\pm 5 \text{ kJ mol}^{-1}$ . In ending this introduction it is worth emphasizing that ab initio procedures generate far more information than total energies – optimized molecular structures, fundamental vibrational frequencies, dipole moments, polarizabilities, individual orbital energies etc. are routinely obtained [8].

#### COMPUTATIONAL STRATEGY

A large split valence basis set with both *d*- and *p*-polarization functions, 6-311G\*\*, was used throughout, including the geometry optimization steps. The correlation energies were estimated using a second order Møller–Plesset perturbation treatment (MP2) [9]. The calculations were performed with Gaussian 88 [18] or Gaussian 90 [19] implemented on the University of London Cray X-MP/28. For the phosphorus–fluorine species some calculations were performed with the inclusion of *f* polarization functions on the phosphorus atom and with an exponent of 0.6, as recommended by Marsden [20]. All species were closed shell except  $\text{PF}_2$  and  $\text{PO}$ , and for these UHF calculations were performed.

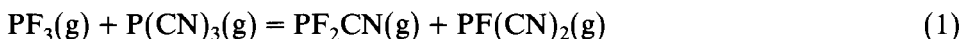
The electronic energies were calculated from the optimized molecular structures even when good quality gas phase structural data were available; for energy calculations it is of pivotal importance that the geometries be internally self-consistent [10].

With the chosen basis set many of the calculations were very long, for example, for the  $\text{P}(\text{CN})_3$  minimization (five SCF cycles), the CPU time was about 3 hours.

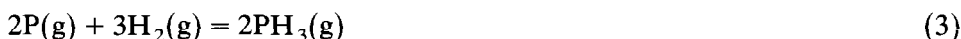
#### RESULTS AND DISCUSSION

Perturbation methods do not reproduce correlation energies exactly; it has been estimated that the MP2 correction represents [7] about half of the total correlation energy. Their merit is that they are very fast computationally compared with configuration interaction calculations. Electron correlation commonly accounts for about 30% of a covalent bond energy, and hence calculations directed at reproducing heats of formation must address

the problem of electron correlation at an early stage. Pople et al. [8] have recommended the use of chemical reactions for energy calculations where there is some cancellation of the electron correlation energy and hence the inability to evaluate it exactly is of lesser consequence. These chemical reactions are of two types and in both total spin is conserved. Isodesmic reactions are reactions where the number of electron pairs is held constant and furthermore, the formal chemical bond types are conserved (for example, eqn. (1)).



Isogyric reactions only conserve the number of electron pairs. For example, eqn. (2) is an isogyric reaction and is suitable reaction for the estimation of  $\Delta H^\circ_f[\text{PH}_3, \text{g}]$  by computational methods, whereas eqn. (3) is not isogyric and its use would lead to large errors in the estimation of  $\Delta H^\circ_f$



#### *Enthalpy of formation of hydrogen cyanide*

Reaction (4) is a convenient isogyric reaction from which to estimate  $\Delta H^\circ_f[\text{HCN}, \text{g}]_{298}$ , as the heat of formation of  $\text{C}_2\text{N}_2$  is well established [21].



The electronic energies ( $U^\circ_0$ ) of each component in eqn. (4) are calculated by the procedures described above, and the value of  $\Delta U^\circ_0$  is converted to  $\Delta H^\circ_{298}$  with eqn. (5)

$$\Delta H^\circ_{298} = \Delta U^\circ_0 + \Delta(\text{ZPE}) + \Delta(H^\circ_{298} - H^\circ_0) \quad (5)$$

The zero-point energies (ZPE) are calculated from  $\frac{1}{2}h\Sigma\nu_i$ , where  $\nu_i$  are fundamental vibrational frequencies and the enthalpy functions ( $H^\circ_{298} - H^\circ_0$ ) are obtained from standard statistical thermodynamic routines assum-

TABLE 1

Energy functions for eqn. (4),  $\text{H}_2 + \text{C}_2\text{N}_2 = 2\text{HCN}$

Species	$U^\circ_0(\text{H})^a$	ZPE <sup>b</sup> (kJ mol <sup>-1</sup> )	$(H^\circ_{298} - H^\circ_0)$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ_f$ (kJ mol <sup>-1</sup> )
$\text{H}_2$	-1.160272	26.3 [23]	8.4 [22]	0
$\text{C}_2\text{N}_2$	-185.296200	40.8 [22]	12.6 [22]	309.1 ± 1.8 [21,22]
HCN	-93.237360	40.9 [22]	9.2 [22]	137 (calcd.)

<sup>a</sup> Hartree = 2625.5 kJ mol<sup>-1</sup>.

<sup>b</sup> The references in this column refer to the source of the fundamental vibrational frequencies; ZPE is calculated from the equation given in the text.

ing a rigid rotor harmonic oscillator model [22]; these quantities are collected in Table 1.

The calculated value for the heat of formation of HCN at 25°C is  $137 \pm 10 \text{ kJ mol}^{-1}$ ; the uncertainty interval is estimated (see introduction) and includes uncertainty in the heat of formation of  $\text{C}_2\text{N}_2$  (see Table 1). The experimental enthalpy of formation of HCN is  $135 \pm 8 \text{ kJ mol}^{-1}$  and is based on early combustion calorimetry by Berthelot [6] and Thomsen [24]. Berthelot [6] detonated a mixture of HCN and  $\text{O}_2$  contained in a combustion bomb equilibrated at 18°C. The quantities of HCN were chosen so that all of the HCN was in the vapour phase despite the normal boiling point of HCN (25.6°C) being higher than the calorimeter operating temperature. Thomsen [24] gives no experimental details. This work, together with some equilibrium studies involving HCN, has been assessed critically and the ancillary data updated to yield the recommended figure of  $135 \pm 8 \text{ kJ mol}^{-1}$  [22,25]. Hence the value from the molecular orbital (M.O.) calculation supports the recommended experimental result.

### *Enthalpy of formation of tricyanophosphine*

There has been little systematic study of phosphorus compounds by M.O. methods, and consequently it is inappropriate to select an isogyric reaction to predict the properties of an unknown phosphorus compound without first validating the chosen wave functions (the basis set) for phosphorus-containing species. Table 2 contains a list of simple phosphorus-containing molecules, their electronic energies by M.O. calculation and their zero point energies: corresponding results for some ancillary molecules are included in this table. Table 3 lists several isogyric reactions involving these species, all of which have known standard enthalpies of formation. The calculated and experimental values for  $\Delta H_{298}^\circ$  for the isogyric reactions are compared in this table.

Reactions 1–4 in Table 3 shows that the chosen basis set (MP2/6-311G\*\*) is able to reproduce heats of formation with a just acceptable accuracy. The predicted heats of formation of the phosphorus–fluorine compounds (reactions 8, 9 and 10) are, however, seriously in error; this error is  $\approx 22 \text{ kJ mol}^{-1}$  per P–F bond suggesting a systematic deviation. Repeating the calculation with additional *f* polarization functions on P improves the accuracy markedly – compare reactions 8 and 9 with 12 and 13 respectively; lack of computational resource did not allow us to perform the calculation for  $\text{PF}_5$  with added *f* functions. To establish that this improvement is not an artefact, a calculation was performed with added *f* functions for a species ( $\text{PH}_3$ ) that is satisfactorily predicted without them. Comparing reactions 1 and 11, it is clear that the added polarization functions in this case have little effect.

TABLE 2

Energy functions for some gaseous phosphorus-containing species and ancillary molecules

Species	$-U_0^{\circ}(H)^a$	ZPE <sup>b</sup> (kJ mol <sup>-1</sup> )	$(H_{298}^{\circ} - H_0^{\circ})^c$ (kJ mol <sup>-1</sup> )	$\Delta H_f^{\circ}$ (kJ mol <sup>-1</sup> )
P <sub>2</sub>	681.932180	8.4	8.7	144.0 ± 2.0 [16]
PH <sub>3</sub>	342.736629	61.1	10.1	5.4 ± 1.7 [22]
PN	395.600123	18.2	8.7	172 ± 15 [26]
PO( <sup>2</sup> Π <sub>1/2</sub> )	416.024453 <sup>d</sup>	7.4	9.4	-23.5 ± 4.2 [22]
P <sub>2</sub> H <sub>4</sub>	684.298273	99.7 <sup>e</sup>	12.8 <sup>f</sup>	20.9 ± 4.2 [26]
PF <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> )	540.353328 <sup>d</sup>	12.2	11.2	-482 ± 21 [27]
PF <sub>3</sub>	640.124242	22.6	12.9	-957.3 ± 1.3 [22]
PF <sub>5</sub>	839.547982	44.7	16.5	-1593.3 ± 1.2 [28]
P(CN) <sub>3</sub>	618.925491	67.2 <sup>g</sup>	21.2 <sup>h</sup>	see text
PH <sub>2</sub> CN	434.805400	73.2 <sup>e</sup>	11.6 <sup>k</sup>	see text
PH <sub>3</sub>	342.752829 <sup>i</sup>			
PF <sub>2</sub>	540.391112 <sup>i</sup>			
PF <sub>3</sub>	640.177497 <sup>i</sup>			
P <sub>2</sub>	681.968666 <sup>i</sup>			
H <sub>2</sub> <sup>j</sup>	1.160272	26.3	8.4	0
N <sub>2</sub> <sup>j</sup>	109.334060	14.1	8.7	0
O <sub>2</sub> <sup>j</sup>	150.060825	4.2	9.0	0
F <sub>2</sub> <sup>j</sup>	199.193333	5.5	8.8	0

<sup>a</sup> Ground state vibrationless electronic energy at 0 K in Hartree (2625.5 kJ mol<sup>-1</sup>).<sup>b</sup> The ZPE were calculated (see text) from the fundamental vibrational frequencies ( $\nu_i$ ) and these were obtained (unless indicated otherwise) from ref. 23 (diatomics) or ref. 22 (polyatomics).<sup>c</sup> The structural data required in addition to  $\nu_i$  to calculate this function were taken from refs. 22 and 23 unless indicated otherwise.<sup>d</sup> Both these species are spin doublets and the M.O. calculations were UHF; all others were RHF.<sup>e</sup>  $\nu_i$  values were obtained from a harmonic analysis sub-routine of Gaussian 90 employing analytical gradients for the first and second derivatives of the SCF energy, the MP2 component was not included at this stage.<sup>f</sup> Calculated from  $\nu_i$  (footnote e) and structural constants from the optimized Gaussian 90 geometry ( $r_{PP} = 2.23$  Å,  $r_{PH} = 1.41$  Å, HPH = 94°, PPH = 97°)<sup>g</sup> Calculated using  $\nu_i$  from Edwards et al. [29]; the single inactive frequency ( $A_2$ ) was estimated as 385 cm<sup>-1</sup>.<sup>h</sup> Calculated using the solid state structural data from Emerson and Brotton [30].<sup>i</sup> These values of  $U_0^{\circ}$  were calculated with the inclusion of the  $f$  polarization functions (see the section headed Computational strategy).<sup>j</sup> Ancillary species.<sup>k</sup> From the optimized geometry.

Both PF<sub>3</sub> and PF<sub>5</sub> have been studied previously by ab initio M.O. methods [20,31,32]. Neither study was undertaken to derive energetic data, rather to develop a harmonic force field with which to interpret spectroscopic and structural properties. In both studies, extensive use was made of

TABLE 3

Standard enthalpies of formation of some phosphorus compounds at 298.15 K from the energy changes in isogyric reactions

No.	Species	Reaction	$\Delta H_f^\circ(\text{calc})$ (kJ mol <sup>-1</sup> )	$\Delta H_f^\circ(\text{lit}^a)$ (kJ mol <sup>-1</sup> )	$\Delta^b$ (kJ mol <sup>-1</sup> )
1	PH <sub>3</sub>	P <sub>2</sub> + 3H <sub>2</sub> = 2PH <sub>3</sub>	+3.4	5.4 ± 1.7	2
2	PN	P <sub>2</sub> + N <sub>2</sub> = 2PN	+165.5	172 ± 15	7
3	PO	<sup>c</sup> P <sub>2</sub> + O <sub>2</sub> = 2PO	+0.3	-23.5 ± 4.2	-24
4	P <sub>2</sub> H <sub>4</sub>	P <sub>2</sub> + 2H <sub>2</sub> = P <sub>2</sub> H <sub>4</sub>	+50.3	20.9 ± 4.2	-29
5	P(CN) <sub>3</sub>	P <sub>2</sub> + 3C <sub>2</sub> N <sub>2</sub> = 2P(CN) <sub>3</sub>	+496	-	-
6	P(CN) <sub>3</sub>	PH <sub>3</sub> + 3HCN = P(CN) <sub>3</sub> + 3H <sub>2</sub>	+493	-	-
7	P(CN) <sub>3</sub>	P <sub>2</sub> + 6HCN = 2P(CN) <sub>3</sub> + 3H <sub>2</sub>	+491	-	-
8	PF <sub>2</sub>	<sup>c</sup> P <sub>2</sub> + 2F <sub>2</sub> = 2PF <sub>2</sub>	-437	-482 ± 21	-45
9	PF <sub>3</sub>	P <sub>2</sub> + 3F <sub>2</sub> = 2PF <sub>3</sub>	-889	-957.3 ± 1.3	-68
10	PF <sub>5</sub>	P <sub>2</sub> + 5F <sub>2</sub> = 2PF <sub>5</sub>	-1483	-1593.3 ± 1.2	-110
11	PH <sub>3</sub> (f) <sup>d</sup>	P <sub>2</sub> (f) + 3H <sub>2</sub> = 2PH <sub>3</sub> (f)	+8.8	5.4 ± 1.7	-3
12	PF <sub>2</sub> (f) <sup>d</sup>	<sup>c</sup> P <sub>2</sub> (f) + 2F <sub>2</sub> = 2PF <sub>2</sub> (f)	-488	-482 ± 21	6
13	PF <sub>3</sub> (f) <sup>d</sup>	P <sub>2</sub> (f) + 3F <sub>2</sub> = 2PF <sub>3</sub> (f)	-981	-957.3 ± 1.3	-24
14	PH <sub>2</sub> CN	P <sub>2</sub> + 2H <sub>2</sub> + C <sub>2</sub> N <sub>2</sub> = 2PH <sub>2</sub> CN	+160	-	-

<sup>a</sup> The literature sources for the heats of formation are given in Table 2.

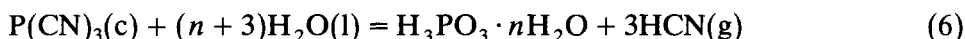
<sup>b</sup>  $\Delta$  (kJ mol<sup>-1</sup>) =  $\Delta H_f^\circ(\text{lit}) - \Delta H_f^\circ(\text{calc})$

<sup>c</sup> Notice that these two reactions are not strictly isogyric because they include radicals.

<sup>d</sup> Calculation performed with  $U_0$  including  $f$  polarization functions (see Table 2).

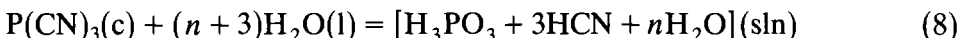
polarization functions, but not at the  $f$  level. Fluorine compounds constitute a demanding test of ab initio methods directed to the prediction of energetic data; early M.O. studies on F<sub>2</sub> showed the molecule to be unbound at the Hartree–Fock limit, and recent studies [33] on small molecular species require large basis sets and elaborate correlation energy procedures to predict energetic data adequately. Given this background, it is unsurprising that additional polarization functions were required in this work to reproduce satisfactorily the heats of formation of the phosphorus fluorides. The mean absolute deviation between the calculated and experimental heats of formation for six phosphorus-containing molecules (reactions 1–4, 12 and 13 in Table 3) is 15 kJ mol<sup>-1</sup>; this may be regarded as a satisfactory validation of the chosen basis set and prediction of heats of formation of other phosphorus-containing species may be undertaken at this level of confidence.

In Table 3, reactions 5–7 are three isogyric reactions involving P(CN)<sub>3</sub>, of which only two are mutually independent. From these reactions we may assert  $\Delta H_f^\circ[(\text{PCN})_3, \text{g}]_{298} = 493 \pm 15$  kJ mol<sup>-1</sup>. The original experimental study [1] (see Introduction) yielded  $569 \pm 24$  kJ mol<sup>-1</sup> for the same quantity from a thermodynamic examination of reactions (6) and (7)





The calorimetric liquid in (6) was presaturated with  $\text{HCN}(\text{g})$  and it was assumed that the liberated  $\text{HCN}$  from the hydrolysis was gaseous. A reappraisal [3] of this reaction indicates that this assumption was almost certainly incorrect; the  $\text{HCN}$  ( $T_b = 25.6^\circ\text{C}$ ) was liberated as  $\text{HCN}(\text{l})$  and is probably completely miscible [34] with the hydrolysate.  $\text{HCN}$  ( $\text{p}K_a = 8.7$  at  $25^\circ\text{C}$ ) is a weak acid and the  $\text{H}_3\text{PO}_3$  present in the hydrolysate further suppresses ionization. Consequently the hydrolysis reaction studied in the 1976 work was probably reaction (8).



The difference between  $\Delta H_f^\circ[\text{HCN}, \text{g}]$  and  $\Delta H_f^\circ[\text{HCN}, \text{aq, unionized}]$  is  $28.0 \text{ kJ mol}^{-1}$  [25]. Making this single correction to the 1976 study [1] we obtain  $\Delta H_f^\circ[\text{P}(\text{CN})_3, \text{g}] = 485 \pm 25 \text{ kJ mol}^{-1}$ . Some preliminary combustion calorimetry [3] with  $\text{P}(\text{CN})_3(\text{c})$  in a rotating oxygen bomb yielded a heat of formation of ca.  $440 \text{ kJ mol}^{-1}$ ; adding the enthalpy of sublimation [1] gives a corresponding value for the gas phase of  $516 \text{ kJ mol}^{-1}$ . It is now clear that the three independent values of  $\Delta H_f^\circ[\text{P}(\text{CN})_3, \text{g}]$ , from M.O. studies ( $493 \pm 15 \text{ kJ mol}^{-1}$ ), from a reappraisal of the reaction calorimetry ( $485 \pm 25 \text{ kJ mol}^{-1}$ ) and from preliminary rotating bomb calorimetry ( $\approx 516 \text{ kJ mol}^{-1}$ ) are in approximate agreement.

During the search for optimum starting conditions for the  $\text{P}(\text{CN})_3$  minimization, the unknown species  $\text{PH}_2\text{CN}$  was examined by the M.O. methods discussed herein. The results are included in Table 2 and an isogyric reaction (No. 14) is given in Table 3 from which  $\Delta H_f^\circ[\text{PH}_2\text{CN}, \text{g}] = +160 \text{ kJ mol}^{-1}$ . This is a simple example of the use of ab initio methods in the calculation of thermodynamic data for unknown or unstable species.

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