583. *Heats of Formation and Bond Energies. Part I. Trisdiethylaminophosphine.*

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The heat of reaction between an excess of diethylamine and phosphorus trichloride in cyclohexane, to give trisdiethylaminophosphine, has been measured, *viz.*, $\Delta H_f^\circ[(Et_2N)_3P, \text{liq.}] = -66{\cdot}8 \pm 2{\cdot}5$ kcal./mole. The mean bond energy term, $\bar{E}(P-N) = 66{\cdot}8 \pm 0{\cdot}8$ kcal./mole, is derived. Also the value $\Delta H_f^\circ(Et_2NH,HCl, \text{cryst.}) = -85{\cdot}6 \pm 0{\cdot}2$ kcal./mole is found.

The purposes of this series of papers are to report the measurement of heats of formation of compounds, from these to derive bond-energy terms and bond-dissociation energies, and to investigate deviation of these quantities from additivity. The first group to be considered are organophosphorus compounds, and this paper deals with a compound containing phosphorus–nitrogen bonds.

Recent papers on the thermochemistry of phosphorus compounds have dealt mainly with phosphorus–carbon,[1] phosphorus–oxygen,[2] and phosphorus–halogen [3,4] bonds in tervalent phosphorus compounds, and in phosphoryl and thiophosphoryl compounds with the effects of different groups bonded to the phosphorus atom.[5-8]

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[1] Long and Sackmann, *Trans. Faraday Soc.*, 1957, **53**, 1606.
[2] Chernick, Skinner, and Mortimer, *J.*, 1955, 3936.
[3] Charnley and Skinner, *J.*, 1953, 450.
[4] Neale and Williams, *J.*, 1952, 4535; 1954, 2156.
[5] Chernick and Skinner, *J.*, 1956, 1401.
[6] Neale and Williams, *J.*, 1955, 2485.
[7] *Idem*, *J.*, 1956, 422.
[8] Chernick, Pedley, and Skinner, *J.*, 1957, 1851.

There is little thermochemical information about tervalent organophosphorus compounds containing phosphorus–nitrogen bonds, although for quinquevalent compounds the heats of formation of two alkylphosphonic dianilides are known.[7]

In an inert solvent, at room temperature, phosphorus trichloride reacts with a secondary amine, present in excess, to give an aminophosphine.[9] In cyclohexane, diethylamine reacts thus:

$$PCl_3(liq.) + 6Et_2NH(soln.) \longrightarrow (Et_2N)_3P(soln.) + 3Et_2NH,HCl(cryst.) \quad . \quad (1)$$

to give trisdiethylaminophosphine in solution and a precipitate of crystalline diethylamine hydrochloride.

With phosphorus oxychloride, triamino-derivatives are formed by reaction with secondary amines only at elevated temperatures.[10] At room temperature, in an inert solvent, one or two of the chlorine atoms are replaced by amino-groups. In cyclohexane, reaction with diethylamine gives a mixture of dichlorodiethylaminophosphine oxide and chlorobisdiethylamidophosphine oxide, and the reaction was found to be unsuitable for thermochemical study.

A secondary, rather than a primary, amine was chosen so as to avoid complication due to the possible formation of imides R·N=P·NHR [11] and R·N=PO·NHR.[12]

EXPERIMENTAL

Materials.—Cyclohexane (Howard, Ilford) was distilled, in dry nitrogen, from calcium hydride, immediately before use. Phosphorus trichloride (B.D.H. Laboratory Reagent) was distilled, in dry nitrogen, through a 6″ Fenske column, and had b. p. 74·4—74·6°/746 mm. It was redistilled *in vacuo* and sealed in thin, weighed glass phials. Diethylamine (B.D.H. Laboratory Reagent) was distilled, from calcium hydride, through an 18″ Fenske column; it had b. p. 54·7°/750 mm.

Trisdiethylaminophosphine was prepared by the addition of phosphorus trichloride (60 g., 0·42 mole) in ether (200 ml.) to diethylamine (210 g., 3·0 moles) in ether (1·5 l.). The precipitated amine hydrochloride was removed by filtration, then the ether by distillation, and the triaminophosphine was distilled under reduced (nitrogen) pressure, through a 6″ Fenske column. It had b. p. 85·0°/2 mm. Michaelis [10] gives b. p. 80—90°/10 mm.

Calorimeter.—The heats of reaction were measured in a calorimeter similar to that described by Pedley *et al.*[13]. It consisted of a cylindrical, silvered Dewar vessel (capacity 300 ml.) encased in a brass can fitted with a flanged brass lid, which was totally immersed in a thermostat bath at 25·000° ± 0·005°. Heavy brass chimneys in the calorimeter lid allowed entrance into the Dewar vessel of the stirrer (480 r.p.m.) and an electrical heater and thermistor element, both encased in glass tubes, and a glass rod holding a phial of reactant. The whole system, together with electrical equipment, was housed in a constant-temperature room at 25·0° ± 0·2°. The Dewar vessel was charged with a solution of diethylamine (39·5 g.) in cyclohexane (145·0 g.) which was kept under a slight positive pressure of dry nitrogen, to prevent ingress of moisture. When a steady state was reached thermally, the phial of phosphorus trichloride was crushed. With a molar ratio of $PCl_3 : Et_2NH$ of 1 : 10 the reaction still continued after 60 min. The mole ratio used was 1 : 200, the reaction being complete in ~15 min. The calorimeter was calibrated electrically by the substitution method.

Units.—Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. joule.

Results.—In the reactions with phosphorus trichloride the precipitated diethylamine hydrochloride was recovered, in amount at least 99·8% of that required by reaction (1).

[9] Kosolapoff, "Organo-phosphorus Compounds," Chapman and Hall, Ltd., London, 1950, p. 278.

[10] Michaelis, *Annalen*, 1903, **326**, 129.

[11] Grimmel, Guenther, and Morgan, *J. Amer. Chem. Soc.*, 1946, **68**, 539.

[12] Michaelis, *Annalen*, 1915, **407**, 290; Michaelis and Silberstein, *Ber.*, 1896, **29**, 716.

[13] Pedley, Skinner, and Chernick, *Trans. Faraday Soc.*, 1957, **53**, 1612.

In Table 1, ΔH refers to the observed heat of reaction (1): the mean value is $-103{\cdot}2 \pm 1{\cdot}3$ kcal./mole. The comparatively large standard deviation is attributed to the formation of a precipitate, which may lead to heterogeneity in the final reaction mixture. Heats of solution in cyclohexane–diethylamine solution were measured independently, being Et_2NH(liq.) $+0{\cdot}44 \pm 0{\cdot}03$, and $(Et_2N)_3P$(liq.) $0 \pm 0{\cdot}05$ kcal./mole. With these additional data, the heat is calculated to be $\Delta H_2 = -100{\cdot}6 \pm 1{\cdot}5$ kcal./mole for the idealised reaction (2):

TABLE 1.

PCl_3 (g.)	0·2746	0·2804	0·2853	9·2666	0·2650	0·2969	0·2529	0·2694
$-\Delta H$ (kcal./mole)	99·5	108·0	102·1	103·6	108·2	100·2	102·7	101·3

$$PCl_3(\text{liq.}) + 6Et_2NH(\text{liq.}) \longrightarrow (Et_2N)_3P(\text{liq.}) + 3Et_2NH,HCl(\text{cryst.}) \quad . \quad . \quad (2)$$

Heats of Formation.—The heat of formation of the aminophosphine is related to the corresponding ΔH_2 through the thermochemical equation:

$$\Delta H_f°[(Et_2N)_3P, \text{liq.}] = \Delta H_2 + \Delta H_f°(PCl_3, \text{liq.}) - 3\Delta H_f°(Et_2NH,HCl, \text{cryst.}) + 6\Delta H_f°(Et_2NH, \text{liq.})$$

The value $\Delta H_f°(PCl_3, \text{liq.}) = -74{\cdot}4$ kcal./mole (ref. 4) is accepted here, together with $\Delta H_{\text{vap.}} = 7{\cdot}8$ kcal./mole (ref. 14), which gives $\Delta H_f°(PCl_3, \text{g.}) = -66{\cdot}6$ kcal./mole. A recent determination of the heat of combustion of liquid diethylamine[15] gives $\Delta H_c° = -727{\cdot}2 \pm 0{\cdot}3$ kcal./mole, and with the usual values, $\Delta H_f°(H_2O, \text{liq.}) = -68{\cdot}3174$ and $\Delta H_f°(CO_2, \text{g.}) = -94{\cdot}0518$ kcal./mole,[14] gives $\Delta H_f°(Et_2NH, \text{liq.}) = -24{\cdot}8 \pm 0{\cdot}3$ kcal./mole. [Incorporating the latent heat of vaporisation, $\Delta H_{\text{vap.}} = 7{\cdot}8$ kcal./mole, obtained from Jordan's vapour pressure data,[16] we calculate $\Delta H_f°(Et_2NH, \text{g.}) = -17{\cdot}0$ kcal./mole.]

The heat of formation of crystalline diethylamine hydrochloride was determined by two methods. In the first, diethylamine was dissolved in excess of 0·2N-hydrochloric acid:

$$Et_2NH(\text{liq.}) + HCl\ (223H_2O) + \text{Excess of acid solution} \longrightarrow Et_2NH,HCl\ (\text{in acid solution})$$
$$\Delta H = -20{\cdot}50 \pm 0{\cdot}10 \text{ kcal./mole}$$

The heat of solution of crystalline diethylamine hydrochloride in excess of 0·2N-hydrochloric acid was also measured:

$$Et_2NH,HCl(\text{cryst.}) + \text{Excess of acid solution} \longrightarrow Et_2NH,HCl\ (\text{in acid solution})$$
$$\Delta H = +0{\cdot}65 \pm 0{\cdot}03 \text{ kcal./mole}$$

Whence, by using $\Delta H_f°(HCl,223H_2O) = -39{\cdot}81$ kcal./mole[14] and $\Delta H_f°(Et_2NH, \text{liq.})$ derived above, $\Delta H_f°(Et_2NH,HCl, \text{cryst.}) = -85{\cdot}76 \pm 0{\cdot}33$ kcal./mole.

In the second method diethylamine hydrochloride was dissolved in excess of 0·2N-sodium hydroxide:

$$Et_2NH,HCl(\text{cryst.}) + NaOH(223H_2O) + \text{Excess of alkali} \longrightarrow (Et_2NH + NaCl + H_2O)\ (\text{in alkaline solution})$$
$$\Delta H = -0{\cdot}33 \pm 0{\cdot}03 \text{ kcal./mole}$$

The heat of solution of liquid diethylamine in excess of 0·2N-sodium hydroxide was also measured:

$$Et_2NH(\text{liq.}) + \text{Excess of alkaline solution} \longrightarrow Et_2NH\ (\text{in alkaline solution})$$
$$\Delta H = -7{\cdot}53 \pm 0{\cdot}05 \text{ kcal./mole.}$$

The following additional data are used:

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[14] National Bureau of Standards, Circular 500, Washington, D.C., 1952.

[15] Prosen, National Bureau of Standards, Washington D.C., personal communication.

[16] Jordan, " Vapor Pressure of Organic Compounds," Interscience Publ. Inc., London, 1954, p. 179.

$\Delta H_f^\circ(\text{NaOH},223\text{H}_2\text{O}) = -112{\cdot}10$, and $\Delta H_f^\circ(\text{NaCl},223\text{H}_2\text{O}) = -97{\cdot}21$ kcal./mole:[14] here the assumption is made that the heat of solution of crystalline sodium chloride to this dilution is the same in water as in 0·2N-sodium hydroxide. From these data we calculate $\Delta H_f^\circ(\text{Et}_2\text{NH,HCl, cryst.}) = -85{\cdot}42 \pm 0{\cdot}38$ kcal./mole. The two methods give results in close agreement, which serves as a check on the calibration of the calorimeter. We take $\Delta H_f^\circ(\text{Et}_2\text{NH,HCl, cryst.}) - \Delta H_f^\circ(\text{Et}_2\text{NH, liq.}) = -60{\cdot}80 \pm 0{\cdot}15$ kcal./mole.

From these data and ΔH_2, we derive $\Delta H_f^\circ[(\text{Et}_2\text{N})_3\text{P, liq.}] = -66{\cdot}8 \pm 2{\cdot}5$ kcal./mole.

The vapour pressure of this compound has been measured and is given by the equation $\log_{10} p(\text{mm.}) = -A/T + B$, where $A = 3171$ and $B = 8{\cdot}80$. The derived latent heat of vaporisation (liquid to vapour), given by $\Delta H_{\text{vap.}} = -4{\cdot}57A \times 10^{-3}$ kcal./mole, is $14{\cdot}5 \pm 0{\cdot}1$ kcal./mole.

Incorporating these values gives $\Delta H_f^\circ[(\text{Et}_2\text{N})_3\text{P, g.}] = -52{\cdot}3 \pm$ kcal./mole.

DISCUSSION

The first step in deriving bond-energy terms is to calculate the heat of formation of the gaseous compound from the atoms, $\Delta H_f^a(\text{g.})$.

This may be obtained from the relation:

$$\Delta H_f^a(\text{g.}) = \Delta H_f^\circ(\text{g.}) - \Sigma\Delta H_a,$$

where $\Delta H_f^\circ(\text{g.})$ is the heat of formation of the gaseous compound from the elements and the ΔH_a terms are the heats of atomisation of the elements at 25°. Values used are: C, 170·89;[17] H, 52·09;[14] O, 59·54; N, 112·9; P, 75·3; and Cl, 28·94 kcal./g.-atom.[18]

From the $\Delta H_f^\circ(\text{g.})$ values above and $\Delta H_f^\circ(\text{POCl}_3\text{, g.}) = -134{\cdot}3$ kcal./mole (ref. 3), the $\Delta H_f^a(\text{g.})$ terms are calculated: PCl_3, $-228{\cdot}72$; POCl_3, $-355{\cdot}96$; $(\text{Et}_2\text{N})_3\text{P}$, $-4079{\cdot}7$; and Et_2NH, $-1386{\cdot}45$ kcal./mole. The group energy term, $\bar{E}(\text{Et}_2\text{N})$, the sum of the bond-energy terms in the group, is evaluated from $\bar{E}(\text{Et}_2\text{N}) = -\Delta H_f^a(\text{Et}_2\text{NH, g.}) - \bar{E}(\text{N–H})$. Taking $\bar{E}(\text{N–H}) = 93{\cdot}4$ kcal./mole we have $\bar{E}(\text{Et}_2\text{N}) = 1293{\cdot}05$ kcal./mole. Since $\Delta H_f^a[(\text{Et}_2\text{N})_3\text{P, g.}] = 3\bar{E}(\text{Et}_2\text{N}) + 3\bar{E}(\text{P–N})$, we derive $\bar{E}(\text{P–N}) = 66{\cdot}8 \pm 0{\cdot}8$ kcal./mole. Also, since $-\Delta H_f^a(\text{PCl}_3\text{, g.}) = 3\bar{E}(\text{P–Cl})$, we obtain $\bar{E}(\text{P–Cl}) = 76{\cdot}2$ kcal./mole.

For phosphoryl compounds the situation is less simple. It has been suggested[5] that the OPR_3 molecule should be regarded as a tetrahedral structure, $^-\text{O}–^+\text{PR}_3$, modified by back co-ordination from the $2p_{x^2}$ and $2p_{y^2}$ orbitals of O^- to the vacant $3d_\pi$ orbitals of P^+, thus giving $^-\text{O}–\text{P}^+$ triple-bond character, with the further possibility of back co-ordination to P from the R atoms or groups if these have donor electrons.

Oxidation of the compound PR_3 to OPR_3 is accompanied by a number of energy changes. (i) The promotional energy of the phosphorus atom from the tervalent to the quinquevalent state. (ii) The energy of formation of the phosphoryl bond, which is not constant from one molecule to another, as suggested by the shift in the Raman frequency and infrared wavelength of the phosphoryl bond, on changing the R groups.[19] (iii) The energy change accompanying alteration in the P–R bond character, *e.g.*, as indicated by a shortening of the P–Cl bond length of 2·04 Å, in phosphorus trichloride,[20] to 1·99 Å in phosphorus oxychloride,[21] suggesting a strengthening of this bond on oxidation.

A measure of the energy changes on oxidation is the heat of dissociation, $D(\text{P=O})$, of the molecule OPR_3 in the gaseous state, $\text{OPR}_3(\text{g.}) \longrightarrow \text{O}(\text{g.}) + \text{PR}_3(\text{g.})$. It is given by the thermochemical equation:

$$D(\text{P=O}) = \Delta H_f^\circ(\text{PR}_3\text{, g.}) - \Delta H_f^\circ(\text{OPR}_3\text{, g.}) + \Delta H_f^\circ(\text{O, g.})$$

[17] Brewer and Searcy, *Ann. Rev. Phys. Chem.*, 1956, **7**, 259.

[18] Cottrell, " The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 2nd Edn., 1958.

[19] Williams, Gordy, and Sheridan, *J. Chem. Phys.*, 1952, **20**, 164.

[20] Kisliuk and Townes, *Phys. Rev.*, 1950, **78**, 347.

[21] Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.

and is a quantity of physical significance in that, at least in theory, it is capable of direct measurement. For phosphorus oxychloride we have $D(\text{P=O}) = 127{\cdot}2$ kcal./mole. Similarly, from $\Delta H_f^\circ(\text{P}_4\text{O}_6,\ \text{g.})$ and $\Delta H_f^\circ(\text{P}_4\text{O}_{10},\ \text{g.})$, the value $D(\text{P=O}) = 115$ kcal./mole has been calculated.[6] Although $\Delta H_f^\circ[(\text{Et}_2\text{N})_3\text{P},\ \text{g.}]$ is known, the corresponding $\Delta H_f^\circ[(\text{Et}_2\text{N})_3\text{PO},\ \text{g.}]$ is unknown, and $D(\text{P=O})$ cannot be obtained in this case.

An alternative, though less fundamental, approach is to calculate bond-energy terms, and this depends on apportioning the total energy change on oxidation. Here the energy changes (i) and (ii) are assumed to be constant from one molecule to another, identified with the bond-energy term, $\bar{E}(\text{P=O})$, and given an arbitrary value of 115·0 kcal./mole.[6] From the relation $-\Delta H_f^a(\text{POCl}_3,\ \text{g.}) = 3\bar{E}(\text{P–Cl}) + \bar{E}(\text{P=O})$, we calculate $\bar{E}(\text{P–Cl}) = 80{\cdot}3$ kcal./mole, some 4·1 kcal./mole greater than for this bond in phosphorus trichloride. Neale and Williams [6] have previously calculated $\bar{E}(\text{P–Cl}) = 80$ kcal./mole, in phosphorus oxychloride, using slightly different heats of atomisation given in N.B.S. Circular 500.[14]

Neale and Williams [7] measured the heat of the reaction between alkylphosphonic dichlorides and aniline, in cyclohexane solution, and derive the following thermochemical relation:

$$\Delta H_f^\circ(\text{MePOCl}_2,\ \text{cryst.}) - \Delta H_f^\circ[\text{MePO(Ph·NH)}_2,\ \text{cryst.}] = -62{\cdot}2 \pm 1{\cdot}0$$

$$\Delta H_f^\circ(\text{EtPOCl}_2,\ \text{liq.}) - \Delta H_f^\circ[\text{EtPO(Ph·NH)}_2,\ \text{cryst.}] = -57{\cdot}7 \pm 1{\cdot}0 \text{ kcal./mole.}$$

If it can be assumed that the latent heats of sublimation of the dichloride and corresponding dianilide are the same within $\pm 1{\cdot}0$ kcal./mole, as seems likely, and that $\Delta H_{\text{fusion}}(\text{EtPOCl}_2) = 3{\cdot}0$ kcal./mole, then we calculate

$$\Delta H_f^a(\text{MePOCl}_2,\ \text{g.}) - \Delta H_f^a[\text{MePO(PhNH)}_2,\ \text{g.}] = +2781{\cdot}5$$

$$\Delta H_f^a(\text{EtPOCl}_2,\ \text{g.}) - \Delta H_f^a[\text{EtPO(PhNH)}_2,\ \text{g.}] = +2783{\cdot}0 \text{ kcal./mole.}$$

From the relation:

$$\Delta H_f^a(\text{MePOCl}_2,\ \text{g.}) - \Delta H_f^a[\text{MePO(PhNH)}_2,\ \text{g.}] = 2\bar{E}(\text{Ph·NH}) + 2\bar{E}(\text{P–N}) - 2\bar{E}(\text{P–Cl}),$$

the bond-energy term $\bar{E}(\text{P–N})$ may be calculated in terms of $\bar{E}(\text{P–Cl})$. The group energy term, $\bar{E}(\text{Ph·NH}) = 1389{\cdot}1$ kcal./mole, is evaluated from $\bar{E}(\text{PhNH}) = -\Delta H_f^a(\text{Ph·NH}_2,\ \text{g.}) - \bar{E}(\text{N–H})$, by taking $\Delta H_f^a(\text{Ph·NH}_2,\ \text{g.}) = -1482{\cdot}5$ kcal./mole. This is derived from $\Delta H_f^\circ(\text{PhNH}_2,\ \text{g.}) = +20{\cdot}4$ kcal./mole, calculated in turn from $\Delta H_c^\circ(\text{Ph·NH}_2,\ \text{g.}) = -823{\cdot}8$ kcal./mole (ref. 22).

Taking $\bar{E}(\text{P–Cl}) = 80{\cdot}3$ kcal./mole, as in phosphorus oxychloride, we obtain $\bar{E}(\text{P–N}) = 82{\cdot}0 \pm 2{\cdot}0$ and $82{\cdot}5 \pm 2{\cdot}0$ kcal./mole, where R = Me and Et, respectively. These values are some 15—16 kcal./mole greater than in the aminophosphine.

TABLE 2.

	Tervalent		Phosphoryl *		
Bond	Compound	$\bar{E}$(P–R)	Compound	$\bar{E}$(P–R)	$\Delta\bar{E}$
P–F	PF_3	117·0 † ‡	POF_3	121·9 ‡	4·9
P–Cl	PCl_3	76·2 [4]	POCl_3	80·3 [3]	4·1
P–Br	PBr_3	61·7 [3]	POBr_3	65·0 [3]	3·3
P–OR	$(\text{EtO})_3\text{P}$	91·9 [2]	$(\text{EtO})_3\text{PO}$	103·8 [5]	11·9
	$(\text{Pr}^i\text{O})_3\text{P}$	92·3 [6]	$(\text{Pr}^i\text{O})_2\text{P(O)Me}$	102·9 [6]	10·6
P–N	$(\text{Et}_2\text{N})_3\text{P}$	66·8	$(\text{Ph·NH})_2\text{P(O)Me}$	82·0 [7]	15·2
			$(\text{Ph·NH})_2\text{P(O)Et}$	82·5 [7]	15·7

* $\bar{E}$(P=O) being taken as 115·0 kcal./mole. † Refs. are to heats of formation from which $\bar{E}$(P–R) is derived. ‡ Ebel and Bretscher, *Helv. Chim. Acta*, 1929, **12**, 450.

In Table 2 are to be found some bond-energy terms, together with the difference in these terms, $\Delta\bar{E}$, for a particular bond, in phosphoryl and in tervalent phosphorus compounds. Down the series P–F, P–Cl, P–Br, the $\Delta\bar{E}$ values decrease slightly from 4·9 to 3·3 kcal./mole,

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[22] Klages, *Chem. Ber.*, 1949, **82**, 358.

which runs parallel to a decrease in electronegativity [23] from 3·9 (F) through 3·0 (Cl) to 2·8 (Br). Along the series P–F, P–O, P–N, the $\Delta\bar{E}$ values increase considerably from ~5 through ~11 to ~16 kcal./mole, despite a similar decrease in electronegativity to 3·0 for nitrogen. It seems likely that bond strengthening is due to back-co-ordination to the phosphorus atom.

In the series of compounds, $(Me_2N)_nBCl_{3-n}$ and $(EtO)_nBCl_{3-n}$, it has been shown [24] that bond strengthening, due to back-co-ordination to the boron, is very much greater from nitrogen than from oxygen, which is, in turn, greater than from chlorine. This same order is also found in phosphorus compounds.

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[23] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

[24] Skinner and Smith, *J.*, 1954, 3930.