Boiling Points and Boiling Point Numbers of Trivalent Organophosphorus Compounds

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Application of the Kinney equation, b.p. in °C. = 230.14 (total boiling point number)$^{1/3}$ − 543, furnishes satisfactory results in calculations of normal boiling points of 72 trivalent organophosphorus compounds and of 5 compounds with P—NCO but without P—C; the average error is 2.7°. This involves use of typical Kinney values such as carbon, 0.80, and hydrogen, 1.00. Of the 72 trivalent organophosphorus compounds, 26 have hydrogen attached to phosphorus, 35 have halogen attached to phosphorus, and 11 trialkylphosphines and tetraalkyldiphosphines have methyl, ethyl, and vinyl groups only. Sixteen new boiling point numbers for phosphorus, halogen, isocyanate and also aryl, alkaryl, and aralkyl groups serve in these calculations.

ACCEPTABLE RESULTS OCCUR in application of the Kinney equation (*19*):

$$\text{b.p. in }^\circ\text{C.} = 230.14\,(\text{total boiling point number})^{1/3} - 543 \qquad (1)$$

in calculations of the normal boiling points of hydrocarbons (*19*), silanes and organosilicon compounds (*24*), germanes and alkylgermanium compounds (*2*), boranes and alkylboron compounds (*2*), and alkyl derivatives of bivalent sulfur, selenium and tellurium (*2*). In the alkyl derivatives of bivalent sulfur, selenium, and tellurium it is necessary to use typical Kinney values such as C, 0.80, H, 1.00, and side chain methyl, 3.05, to derive eleven values of the boiling point number (b.p.n.) of sulfur in the different configurations, also six values of b.p.n. for selenium and two values of b.p.n. for tellurium. An attempt to derive b.p.n. for sulfur and hydrogen from H_2S, b.p.n. 9.22, and H_2S_2, b.p.n. 18.96, was unsuccessful (*2*), furnishing 9.74 for sulfur and −0.26 for hydrogen.

Similar attempted derivation of b.p.n.s for phosphorus and hydrogen from PH_3, b.p. −87.4° and b.p.n. 7.76, and P_2H_4, b.p. 51.7° and b.p.n. 17.25, furnishes the unacceptable b.p.n.s of 10.37 for phosphorus and −0.87 for hydrogen; a different derivation of b.p.n. is necessary.

Satisfactory results occur through the following method of calculations on trivalent organophosphorus compounds. First, a separation is made according to the number of alkyl groups present, to get the configurations $RP=$, $R_2P—$ and $R_3P—R_4P_2$; later separation according to the number of different halogen (or hydrogen) atoms attached to phosphorus gives the configurations R_2PX and RPX_2. Second, there is manual derivation of the b.p.n. for phosphorus in the three configurations present in RPH_2, R_2PH and $R_3P—R_4P_2$, using the typical Kinney b.p.n.s C, 0.80, H, 1.00, side chain methyl, 3.05, and double bond in $CH_2{=}CHPR_2$, 1.50 (*19*). This derivation excludes cyclic compounds and $ClCH_2CH_2CH_2PH_2$, because of greater uncertainty in the individual b.p. or b.p.n. For example, an observed b.p. of 87.0° (*33*) for $n\text{-}C_4H_9PH_2$ gives the total b.p.n. 20.51; subtraction of 11.00 for eleven hydrogen atoms and 3.20 for four carbon atoms furnishes the b.p.n. 6.31 for phosphorus present as $RP=$.

Data for acyclic compounds and the already derived b.p.n. for phosphorus in the configurations $RP=$ and $R_2P—$ permit calculations of the b.p.n.s for fluorine, chlorine and bromine in these two configurations, except for fluorine in the apparently unknown R_2PF. The phenyl ring appears to be variable in cyclics of the $RP=$ type; $C_6H_5—$ equals 17.75 ± 0.52 in sixteen compounds, upon assumption of the Kinney values C, 0.80, H, 1.00 and side chain methyl, 3.05.

Table I. Boiling Point Numbers of Atoms and Groups[a]

Configurations of Phosphorus				
	R_3P, R_4P_2[b]	$R_2P—$	$RP=$	$P\equiv$
P	5.37 ± 0.35[c]	5.94 ± 0.34	6.28 ± 0.34	6.48[d]
Configurations of Halogen or Isocyanate				
Halogen(oid)	R_2PX	RPX_2	PX_3	
F	...	0.40 ± 0.13	0.20	
Cl	5.88 ± 0.28	5.20 ± 0.17	4.27	
Br	8.68 ± 0.04	8.06 ± 0.18	7.97	
NCO	...	...	7.48	
Configurations of Special Groups				
Group		$RP=$		
C_6H_5		19.75 ± 0.52		
$CH_3C_6H_4$ or $C_6H_5CH_2$		22.55		
$C_2H_5C_6H_4$ or $(CH_3)_2C_6H_3$		25.35		
$n\text{-}C_3H_7C_6H_4$ or $(CH_3)_3C_6H_2$		28.15		

[a] C, 0.80; H, 1.00; side chain CH_3, 3.05; cyclohexyl ring, 2.70; Cl in $—CH_2Cl$, 7.50; double bond in $CH_2{=}CHPR_2$, 1.50. [b] Methyl, ethyl, and vinyl groups only. [c] Root mean square errors. [d] B.p.n. of phosphorus obtained by extrapolation from R_3P, $R_2P—$ and $RP=$ to $P\equiv$.

Table II. Calculations of Boiling Points of Organophosphines

	B.P.N.		B.P., °C.			
Compound	Calcd.	Found	Calcd.	Found	Error	Ref.
CH_3PH_2	12.08	12.14	−14.9	−14	−0.9	(*15*)
$C_2H_5PH_2$	14.88	15.03	23.1	25	−1.9	(*15*)
n-$C_3H_7PH_2$	17.68	17.48	56.5	54.3	2.2	(*23*)
iso-$C_3H_7PH_2$	16.93	16.34	48.0	41	7.0	(*15*)
n-$C_4H_9PH_2$	20.48	20.51	86.7	87.0	−0.3	(*33*)
iso-$C_4H_9PH_2$	19.73	19.72	78.9	78.8	0.1	(*33*)
iso-$C_5H_{11}PH_2$	22.53	22.48	107.0	106.5	0.5	(*15*)
n-$C_7H_{15}PH_2$	28.88	29.67	163.1	169.5	−6.4	(*36*)
n-$C_8H_{17}PH_2$	31.68	31.72	185.2	185.5	−0.3	(*29*)
$ClCH_2CH_2CH_2PH_2$	24.18	24.45	122.5	125	−2.5	(*33*)
$C_6H_5PH_2$	28.03	28.50	156.1	160	−3.9	(*26*)
$C_6H_5CH_2PH_2$	30.83	31.00	178.6	180	−1.4	(*15*)
4-$CH_3C_6H_4PH_2$[a]	30.83	30.76	178.6	178	0.6	(*28*)
4-$C_2H_5C_6H_4PH_2$[a]	33.63	33.65	199.9	200	−0.1	(*26*)
2,4,5-$(CH_3)_3C_6H_2PH_2$[a]	36.43	35.87	219.9	216	3.9	(*26*)
cyclo-$C_6H_{11}PH_2$	26.78	26.83	145.6	146	−0.4	(*16*)
CH_3PCl_2	20.48	19.98	86.7	81.5	5.2	(*20*)
$C_2H_5PCl_2$	23.28	23.43	114.1	115.5	−1.4	(*13*)
n-$C_3H_7PCl_2$	26.08	26.31	139.5	141.5	−2.0	(*13*)
iso-$C_3H_7PCl_2$	25.33	25.74	132.9	136.5	−3.6	(*13*)
n-$C_4H_9PCl_2$	28.88	28.50	163.1	160	3.1	(*12*)
iso-$C_4H_9PCl_2$	28.13	28.02	156.9	156	0.9	(*13*)
n-$C_5H_{11}PCl_2$	31.68	31.52	185.2	184	1.2	(*12*)
iso-$C_5H_{11}PCl_2$	30.93	31.20	179.4	181.5	−2.1	(*13*)
n-$C_6H_{13}PCl_2$	34.48	34.75	206.1	208	−1.9	(*12*)
n-$C_7H_{15}PCl_2$	37.28	37.67	225.8	228.5	−2.7	(*12*)
n-$C_8H_{17}PCl_2$	40.08	40.45	244.6	246	−1.4	(*12*)
$CH_2{=}CHPCl_2$	22.78	22.22	109.4	104	5.4	(*18*)
$C_6H_5PCl_2$	36.23	36.73	218.5	222	−3.5	(*26*)
2-$CH_3C_6H_4PCl_2$[a]	39.23	39.99	239.0	244	−5.0	(*26*)
3-$CH_3C_6H_4PCl_2$[a]	39.23	38.63	239.0	235	4.0	(*26*)
4-$CH_3C_6H_4PCl_2$[a]	39.23	40.14	239.0	245	−6.0	(*26*)
2,4-$(CH_3)_2C_6H_3PCl_2$[a]	42.03	42.00	257.2	257	0.2	(*37*)
2,5-$(CH_3)_2C_6H_3PCl_2$[a]	42.03	41.53	257.2	254	3.2	(*37*)
4-$C_2H_5C_6H_4PCl_2$[a]	42.03	41.06	257.2	251	6.2	(*26*)
2,4,5-$(CH_3)_3C_6H_2PCl_2$[a]	44.83	45.56	274.6	279	−4.4	(*26*)
2,4,6-$(CH_3)_3C_6H_2PCl_2$[a]	44.83	44.73	274.6	274	0.6	(*26*)
4-iso-$C_3H_7C_6H_4PCl_2$[a]	44.08	43.92	270.0	269	1.0	(*26*)
CH_3PBr_2	26.20	26.14	140.5	140	0.5	(*25*)
$C_2H_5PBr_2$	29.00	28.62	164.1	161	3.1	(*25*)
$CH_2{=}CHPBr_2$	28.50	28.99	160.0	164	−4.0	(*25*)
$C_6H_5PBr_2$	42.15	41.85	257.9	256	1.9	(*27*)
CH_3PF_2	10.88	11.21	−33.0	−28	−5.0	(*22*)
$C_2H_5PF_2$	13.68	13.61	7.4	6.5	0.9	(*22*)
n-$C_4H_9PF_2$	19.28	18.94	74.1	70.5	3.6	(*22*)
$(CH_3)_2PH$	14.54	14.72	18.7	21.1	−2.4	(*8*)
$C_2H_5(CH_3)PH$	17.34	17.50	52.7	54.5	−1.8	(*25*)
$(C_2H_5)_2PH$	20.14	20.32	83.2	85	−1.8	(*15*)
n-$C_3H_7(CH_3)PH$	20.14	19.67	83.2	78.2	5.0	(*25*)
iso-$C_3H_7(CH_3)PH$	19.39	19.74	75.3	79	−3.7	(*15*)
n-$C_4H_9(CH_3)PH$	22.94	23.13	110.9	112.7	−1.8	(*25*)
(iso-$C_3H_7)_2PH$	24.24	23.69	123.0	118	5.0	(*15*)
n-$C_4H_9(C_2H_5)PH$	25.74	25.29	136.5	132.5	4.0	(*35*)
(*n*-$C_4H_9)_2PH$	31.34	31.59	182.6	184.5	−1.9	(*14*)
(iso-$C_5H_{11})_2PH$	35.44	35.38	213.0	212.5	0.5	(*15*)
$(CH_3)_2PCl$	19.42	19.67	75.6	78.2	−2.6	(*20*)
$C_2H_5(CH_3)PCl$	22.22	21.91	104.0	101.0	3.0	(*20*)
$(C_2H_5)_2PCl$	25.02	25.29	130.1	132.5	−2.4	(*3, 17*)
(*n*-$C_4H_9)_2PCl$	36.22	35.94	218.5	216.5	2.0	(*17*)
$C_2H_5(CH_3)PBr$	25.02	25.06	130.1	130.5	−0.4	(*34*)
$(C_2H_5)_2PBr$	27.82	27.78	154.4	154	0.4	(*17*)
$(CH_3)_3P$	16.77	16.30	46.1	40.5	5.6	(*14*)
$C_2H_5(CH_3)_2P$	19.57	19.88	77.2	80.5	−3.3	(*14*)
$(C_2H_5)_2CH_3P$	22.37	23.16	105.5	113	−7.5	(*14*)
$(C_2H_5)_3P$	25.17	24.84	131.5	128.5	3.0	(*14*)
$(CH_2{=}CH)_3P$	23.67	23.80	117.8	119	−1.2	(*11*)
$(CH_3)_2(CH_2{=}CH)P$	19.07	18.70	71.9	67.9	4.0	(*18*)
$C_2H_5(CH_2{=}CH)_2P$	24.17	24.02	122.4	121.0	1.4	(*11*)
$(C_2H_5)_2(CH_2{=}CH)P$	24.67	24.53	127.0	125.7	1.3	(*11*)
$(CH_3)_4P_2$	25.94	26.16	138.3	140.2	−1.9	(*7*)
$(C_2H_5)_4P_2$	37.14	36.65	224.9	221.5	3.4	(*17*)
$(C_2H_5)CH_3PP(C_2H_5)CH_3$	31.54	32.18	184.2	189	−4.8	(*25*)

[a] The connection of phosphorus is to carbon atom number one.

In Table I there are new b.p.n.s for phosphorus present as $RP=$, $R_2P—$, $R_3P—R_4P_2$ and $P\equiv$; the b.p.n. for $P\equiv$ involves a nonlinear extrapolation of the first three respective values 5.37, 5.94 and 6.28 to obtain 6.48 for the b.p.n. of $P\equiv$. In Table I there also are new b.p.n.s for halogen present as RPF_2, R_2PCl, $RPCl_2$, R_2PBr and $RPBr_2$ and new b.p.n.s for the phenyl group and six aralkyl and alkaryl groups attached to phosphorus. The b.p.n. of 7.48 for NCO is an average for the five compounds in Table III. Respective b.p.s of −101.15°, 74.2° and 175.3° for PF_3 (*5*), PCl_3 and PBr_3 are the source of the b.p.n.s of fluorine, chlorine, and bromine in the PX_3 type.

All these calculations are manual rather than by computer. The use of the computer requires preliminary subtraction of the portion of the total b.p.n. due to phosphorus before the computer beings the calculations; this subtraction is still impossible.

LIMITATION

Selection of data is necessary, because some large errors exist in published normal b.p.s of trivalent organophosphorus compounds; perhaps the most serious errors involve extrapolations to obtain normal b.p.s. The b.p. of −14° for CH_3PH_2 (*15*) has been selected for Table II, since this b.p. is more consistent with other b.p.s in the acyclic series than is the later b.p. of −17.2° (*9*). The b.p. listed for $(C_2H_5)_2PCl$ in Table II, 132.5°, is the average of the reported b.p. ranges of 131-132° (*3*) and 133-134° (*17*). Complete rejection of all data by Pass, Schindlbauer, and Steininger (*30–32*) is mandatory because of atypically low values such as: for n-$C_4H_9PH_2$ a b.p. of 76° (*32*) against 87.0° (*33*); for n-$C_5H_{11}PH_2$ a b.p. of 104° (*30*) against 114.1° calculated from the b.p.n. 23.28 derived from the data of five other authors. There is also rejection of the b.p. 139.5° (*15*) for (iso—C_4H_9)(iso—C_3H_7)PH upon comparison with the calculated b.p. 147.8°.

There are some limitations with trialkylphosphines; the b.p.n. of phosphorus drops to 3.85 in $(n\text{-}C_3H_7)_3P$ and 2.40 in $(n\text{-}C_4H_9)_3P$. Retention of the b.p.n.s C, 0.80, and H, 1.00, requires limitation of the alkyl group in R_3P and R_4P_2 to the ethyl group or smaller. Also, substituted R_3P derivatives with the phenyl group present (*21*) offer less reliable values of b.p.n. and are not in Table II. There are too few compounds of the type $R_2P—$ in which R is phenyl for adequate statistical study: the same holds for compounds bearing the ClC_6H_4—group.

B.p.n.s fail to fit the following: organophosphines containing oxygen or sulfur; pentavalent phosphorus; numerous perfluoroalkylphosphines like CF_3PCl_2 (*4*); most mixed halides such as PCl_2F, $PClF_2$ (5), PBr_2F and $PBrF_2$ (6).

DISCUSSION OF RESULTS

In Tables II and III the calculated normal b.p.s of 72 selected trivalent organophosphorus compounds and 5 compounds with P—NCO have an average error of 2.7° and a maximum error of 7.5°. Errors exceed 5.0° for only nine compounds.

Use of the Kinney equation with the typical Kinney values and the new b.p.n.s in Table I allows calculation of some yet unknown b.p.s: some random examples are iso—$C_6H_{13}PH_2$; 132.9°, from total b.p.n. 25.33, n—$C_3H_7PF_2$, 42.7°, from total b.p.n. 16.48, and $(n\text{—}C_3H_7)_2PCl$, 177.0°, from total b.p.n. 30.62.

Compared to chlorine and bromine, the b.p.n.s of fluorine in four compounds are relatively quite low. As expected, the b.p.n. of a halogen decreases progressively in the series R_2PX, RPX_2 and PX_3. The b.p.n. for a given halogen in a phosphorus chloride or bromide always exceeds that in the corresponding halide of boron (2) or silicon (*24*) and either equals or exceeds that in the halide of germanium (2).

Table III. Calculations of Boiling Points (P—NCO)

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., °C. Calcd.	B.P., °C. Found	B.P., °C. Error	Ref.
$PF_2(NCO)$	14.36	14.05	16.4	12.3	4.1	(*1*)
$PF(NCO)_2$	21.64	21.68	98.3	98.7	−0.4	(*1*)
$PCl_2(NCO)$	22.50	22.26	106.7	104.4	2.3	(*1*)
$PCl(NCO)_2$	25.71	25.52	136.3	134.6	1.7	(*1*)
$P(NCO)_3$	28.92	29.65	163.4	169.3	−5.9	(*10*)

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