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Correlation of the Physical Properties of Organophosphorus Compounds. I. Density, Boiling Point, and the Heat of Evaporation of Phosphines

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The boiling point and density of the phosphines have been correlated by using the quantity $M\rho^2$. The use of such data permits the classification of these compounds into associated and normal liquids. These conclusions are also supported by the study of the heat of evaporation of the phosphines.

The various physical properties of the hydrocarbons and their derivatives are dependent on the number of carbon atoms and are estimated from the intermolecular forces contributed by the different bonds, atoms and groups in the molecule and its molecular weight. Correlations with the number of carbon atoms and the boiling points have been demonstrated for many series of compounds but no attempt has so far been made to examine the triply connected phosphorus compounds. A possible reason for the lack of this study is their extreme reactivity towards atmospheric oxygen. The correlation of their properties is, however, difficult because of the nature of the different substituent groups on a central atom of the second row of the periodic table. Such substituents exert different forces on one another and on the central atom, for the estimation of which there is no satisfactory method available. An attempt has been made here to correlate the boiling point with the molecular weight, density and the heat of evaporation with a view to classify the phosphines into different groups and to see if the different substituents have any effect on the physical properties.

Experimental

The tertiary phosphines Nos. 1 to 13 listed in Table 1 were prepared by the Grignard method. They were purified by one of the four different methods: 1) By precipitating the phosphine as the silver iodide adduct and subsequently decomposing the adduct so formed in vacuo as in the case of Me_3P (No. 1). 2) By precipitating as the carbon disulfide adduct and decomposing the latter by refluxing with an alkaline solution. Phosphines Nos. 2 to 5 were purified in this way. 3) By distillation under reduced pressure maintaining an atmosphere of nitrogen if and when necessary. Phosphines 6 to 9, 12 and 13 were purified by this method. 4) Phosphines 10 and 11 being aromatic were purified by first preparing their hydrochloride and their subsequent hydrolysis.

The densities of the phosphines were measured by the methods of Fontana and Calvin[1] with slight modifications. The semimicro pyknometer was designed such that the ground end could be stoppered. The vacuum line attachment was fitted with ground glass joints. Pure phosphines were distilled directly into the bulb carrying the pyknometer. An atmosphere of nitrogen was maintained throughout the transfering, thus avoiding oxidation of the phosphines. The vacuum line was slowly evacuated and then nitrogen was introduced. This forced the liquid into the pyknometer which when filled up was transferred to a dry box filled with nitrogen. The pyknometer was stoppered and in order to maintain an inert atmosphere while weighing, was transferred into a tared ampule. The density of the pure liquid at room temperature controlled at 25°C was thus obtained. Ttrimethylphosphine had to be enclosed into a calibrated tube and sealed prior to weighing as it boils at a low temperature. The densities of the silyl phosphines, the primary and secondary phosphines and the phosphine halides are the reported values from the literature.[2-4]

The boiling points of the phosphines have been determined by extrapolation of the vapor pressure data which was obtained by means of an isoteniscope. In the case of high boiling phosphines the boiling point was obtained by the capillary method. The heat of evaporation of phosphines Nos. 1 to 12 in Table 2 have been obtained from the vapour pressure data. The values for the trifluoromethylphosphines were previously obtained[5] and those for the alkyldichlorophosphines and others are from Refs. 2 and 4.

Discussion

The macro-physical properties of a molecule depend not only on the molecular weight but also on its volume and the polarizability. Since the intermolecular forces which govern these properties depend on the distance between them and on their relative orientation[6] much will depend

TABLE 1. BOILING POINT AND THE DENSITY OF PHOSPHINES

Sample No.	Phosphine	T_b	ρ	$M\rho^2$
1	Me_3P	311.5	0.748	42.52
2	Et_3P	401.2	0.80006	75.57
3	Pr_3P	460.5	0.807	104.2
4	Bu_3P	513.5	0.8118	133.2
5	Me_2PhP	465	0.9678	129.2
6	Et_2PhP	494.9	0.9545	151.9
7	Et_2TolP	513	0.9373	158.1
8	$Et_2(4, Et\text{-}C_6H_4)P$	541.3	0.929	167.4
9	$Et_2(2, 5Et_2\text{-}C_6H_3)P$	533	0.9392	180.0
10	Ph_2MeP	567	1.0784	232.6
11	Ph_3P	657	1.1335	336.6
12	$Et_2(4, Br\text{-}C_6H_4)P$	538	1.2886	407.0
13	$Et_2(4, Cl\text{-}C_6H_4)P$	529	1.0708	230.0
14	$(HOCH_2CH_2)_3P$	457	1.053	184.1
15	PH_3	185.6	0.746	18.92
16	PCl_3	351	1.574	340.6
17	PBr_3	445.9	2.852	2205.0
18	$EtPCl_2$	385	1.2485	404.3
19	$PrPCl_2$	407.5	1.1664	201.9
20	$BuPCl_2$	433	1.1341	204.5
21	$AmPCl_2$	457	1.0997	209.1
22	$HexPCl_2$	481	1.0653	212.3
23	$HeptPCl_2$	501.5	1.0636	227.4
24	$OctPCl_2$	520	1.0433	234
25	$PhPCl_2$	495	1.1373	310.7
26	$CH_3C_6H_4PCl_2$	518	1.2661	309.4
27	$C_2H_5C_6H_4PCl_2$	524	1.2266	311.5
28	$PrC_6H_4PCl_2$	542	1.1917	314.0
29	$C_5H_{11}PH_2$	375	0.7796	63.19
30	$C_5H_9PH_2$	394	0.8818	79.31
31	$C_6H_{13}PH_2$	401	0.7909	73.8
32	$C_8H_{17}PH_2$	442	0.8082	95.37
33	$C_9H_{19}PH_2$	460	0.8122	105.5
34	$PhPH_2$	433	1.001	110.2
35	Ph_2PH	553	1.07	213.0
36	$(Me_3Si)_3P$	515	0.8677	188.2
37	$(Me_3Si)_2PH$	443	0.8188	119.3

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[1] B. J. Fontana and M. Calvin, *Ind. Eng. Chem. Anal.*, **14**, 185 (1942).

[2] G. M. Kosolapoff, "Organophosphorus Compounds," J. Wiley & Sons Inc., New York (1950), pp. 30—37.

[3] R. B. Fox, *J. Am. Chem. Soc.*, **72**, 4148 (1950).

[4] B. Buchner and L. B. Lockhart, Jr., *ibid.*, **73**, 755 (1957).

[5] M. A. A. Beg, Ph. D. Thesis, Univ. Brit. Col., 1961.

[6] G. Scatchard, *J. Am. Chem. Soc.*, **56**, 995 (1934).

on how closely the molecules are packed in a spherical shell of a liquid. Such a packing is indicated by the density of the liquid. The boiling points of hydrocarbons, fatty acids, alcohols and esters have been correlated by equation (1):

$$(T_b - t) = K_b \rho^2 M \tag{1}$$

where T_b is the boiling point, t is 20°C, K_b is a constant, ρ is the density, M the molecular weight and $M\rho^2$ is shown to approximate the cohesive energy.[7] This equation may be simplified to

$$T_b = K_b M \rho^2 \tag{2}$$

where K_b is a constant determined by the type of substituent. The triply connected phosphorus compounds may be classified by the use of Eq. (2) into different classes of compounds. The results listed in Tables 1 and 2, shown graphically in Fig. 1 bear out the applicability of this equation to correlate the boiling point of these compounds. The phosphines seem to fall into different classes and these are governed by the equation of the type $y = a + bX^n$ where y is the boiling point, X is $M\rho^2$ and n is the adjustable parameter. It is found that the $M\rho^2$ values of the phosphines increase in the geometrical progression. The primary alkyl and the trialkyl phosphines have $a = -46.5$, $b = 83.15$ and $n = 0.39$; for the dialkylarylphosphines $a = 355.9$, $b = 0.0743$ and $n = 1.5$. The diarylphosphines also follow an equation of this type as is seen from the nature of the curve for this class of compounds. More data will have to be available in order to obtain an equation for the correlation of the boiling point of these phosphines but the curve obtained from the present values has a distinctly different slope compared with the dialkylarylphosphines. The alkyldichlorophosphines, however, follow the equation:

$$y = 3.53X - 279.7$$

and fall on a straight line.

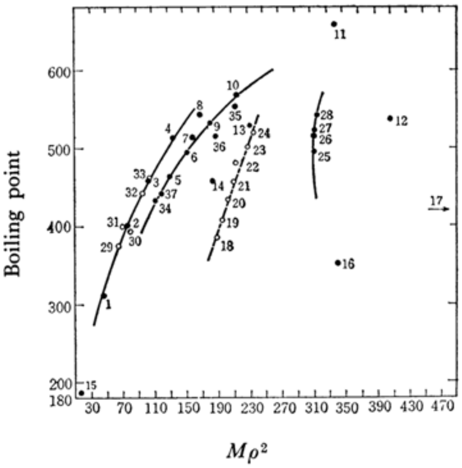

Fig. 1. Correlation of boiling point and density of phosphines.
Curves denote the following order: Mono- and trialkylphosphines, dialkylarylphosphines, alkyldichlorophosphines and aryldichlorophosphines. The numbers follow Table 1.

Table 2. Heat of evaporation of phosphines

Sample No.	Phosphine	L_v (kcal·mol⁻¹)
1	Me_3P	6.94
2	Me_2EtP	7.83
3	Et_3P	9.45
4	Pr_3P	11.17
5	Bu_3P	12.82
6	i-Bu_3P	11.83
7	Me_2PhP	10.38
8	Et_2PhP	12.46
9	Et_2TolP	12.74
10	$Et_2(4,\ Cl\text{-}C_6H_4)P$	13.13
11	$Et_2(4,\ Br\text{-}C_6H_4)P$	14.18
12	Ph_3P	17.00
13	PH_3	3.49
14	Me_2PH	6.27
15	$(CF_3)_3P$	5.89
16	$Me(CF_3)_2P$	6.31
17	Me_2CF_3P	6.95
18	$Ph(CF_3)_2P$	9.05
19	Ph_2CF_3P	11.85
20	$Me_2CH_2{:}\,CHP$	7.75
21	$(CH_2{:}\,CH)_3P$	8.90
22	$EtPCl_2$	8.34
23	$PrPCl_2$	9.36
24	$BuPCl_2$	10.05
25	$AmPCl_2$	10.09
26	$HexPCl_2$	10.83
27	$HeptPCl_2$	11.45
28	$OctPCl_2$	12.26

Correlations among the various classes of phosphines also exist between their boiling point and their molecular weights alone. This is borne out from Fig. 2. The main features of this simple correlation is the separation of the di- and triphenylphosphines from the trialkyl- or dialkylarylphosphines. The type of curves obtained in these two cases is approximately similar to the one obtained earlier. This shows that molecular weight alone is a good parameter for the correlation. While the quantity $M\rho^2$ clearly separates the different classes, molecular weight because of the lack of one of the parameters is not well separated. On both the bases then it is the nature of the substituent on which a classification of the various phosphines is based.

The deviations from the general agreement in

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[7] T. Kotsuka, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, 26 (1960); *Chem. Abstr.*, **54**, 11617 (1960).

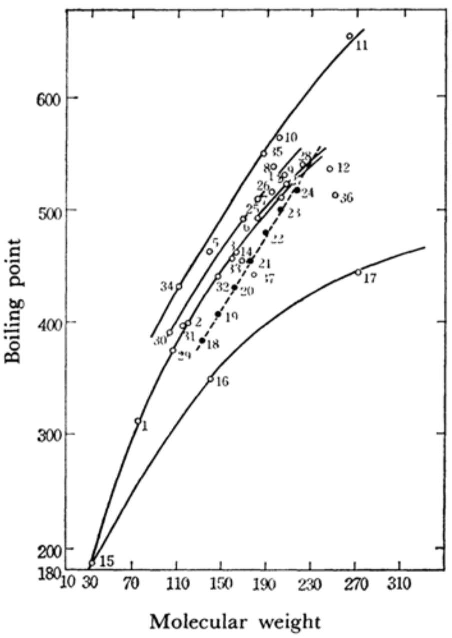

Fig. 2. Correlation boiling point and molecular weight of phosphines.
Curves denote the following order: phenylphosphines, dialkylarylphosphines, aryldichlorophosphines, mono and trialkylphosphines, aryldichlorophosphines, alkyldichlorophosphines.
Numbers follow Table 1.

both cases are for substituents which have an intermediate character. Phosphorus hydride phosphorus(III) chloride and phosphorus(III) bromide are seen to follow one curve. In Fig. 1 this relation is not shown. The trimethylsilylphosphines 36 and 37 and the hydroxyethylphosphine 14 have an intermediate character between the unsubstituted compounds like phosphorus(III) chloride and the alkylphosphines. In Fig. 1 the close relation with alkylphosphines of 37 is well marked. Another group of compounds for which there does not seem to be much agreement is of the aromatic compounds in which there is either halogen substitution as in 12 and 13 or higher alkyl substitution as in 9. However the former are placed near the phosphorus halides while the latter is near the trialkylphosphines. Similar is the case with phenylphosphines 10, 11, 34 and 35 which follow a separate curve in Fig. 2 while in Fig. 1 triphenylphosphine seems to be anomalous.

The different classes, due primarily to the nature of substituents may be explained in terms of the properties of the liquids which may be associated or normal. The difference between the alkyl- and the arylphosphines is clearly marked. On a weight to weight basis, the aromatic compounds have lower volumes than their aliphatic analogues. Their compactness would consequently increase leading to higher cohesive forces. The aliphatic amines and imines are shown to be normal compounds while their aromatic analogues are associated.[8] The enhanced compactness in the cases of aromatic amines, imines and phosphines is possibly brought about by the interaction of the lone pair with the π electrons of the aromatic nucleus. As suggested for the aromatic amines, the aromatic phosphines may also be associated substances. This is further substantiated by the formation of a separate class by the phenylphosphines 10, 11, 34 and 35 which follow a different curve in Fig. 2. The aromatic nucleus having no substituent seems to have a higher interaction of the lone pair with its π electronic cloud.

This type of association is also indicated by the heats of evaporation L_v. Some of these values are listed in Table 2. It may be easily seen that 1) L_v values rise gradually with the chain length, 2) there is an abrupt rise in the case of aryl substitution and 3) there is a marked decrease in the case of trifluoromethyl substitution. The concept of interpenetration[9] may be used to explain the differences in the degree of association among the various phosphines. According to this concept, hydrocarbon melecules interpenetrate one another easily while molecules like those of fluorocarbons do not. The vaporization of interpenetrated molecules thus requires energy to free them from this condition, besides the heat for the change of state. Non-interpenetrated molecules being free require energy only for phase transformation. On this basis it is easy to rationalise the low L_v values for the trifluoromethylphosphines and the methylphosphines. The effect of chain length is clearly demonstrated by the alkyldichlorophosphines. The values of vinyldimethylphosphine and trivinylphosphine are comparable with the corresponding ethylphosphines. This may be explained if the role of π electrons is taken into account. Association promoted by the interaction of the phosphorus lone pair with the aromatic π electrons similarly explains the high values for the aromatic phosphines.

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[8] A. E. Lulski, *Zh. Obschei Khim.*, **26**, 2299 (1956); *Chem. Abstr.*, **51**, 4977 (1957).

[9] H. J. Simons and R. D. Dunlop, *J. Chem. Phys.*, **18**, 335 (1950).