CLXVII.—*The Lower Trialkyl Orthophosphates. Part I.*

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ALTHOUGH fairly complete information respecting some of the physical properties of trimethyl and triethyl orthophosphates is available, little is known concerning those of the other lower alkyl orthophosphates. Boiling points and densities of tri-*n*-propyl, tri*iso*propyl, and tri*iso*butyl phosphates have been recorded, but *tri*-n-*butyl* and *tri*-n-*amyl orthophosphates* have not hitherto been prepared. The preparation and properties of several phosphoric esters have been recently described by Plimmer and Burch (J., 1929, 279, 292). The present series of investigations is confined to the determination of certain physical constants of the lower trialkyl phosphates from methyl to amyl. In view of the paucity and the conflicting character of the results hitherto recorded concerning the physical properties of the phosphoric esters, it was considered advisable to carry out new measurements.

EXPERIMENTAL.

The phosphates were prepared by the action of phosphorus oxychloride on the sodium alkoxides. For instance, in the preparation of *tri*-n-*butyl orthophosphate*, sodium *n*-butoxide was first made by adding gradually 46 g. of sodium to 600 c.c.of *n*-butyl alcohol and then distilling off the excess of alcohol under reduced pressure. To the butoxide, 200 c.c. of dry ether were added, and 60 c.c. of phosphorus oxychloride in 100 c.c. of ether were run in with ice-cooling. The mixture was then boiled gently for an hour, water added, and the ethereal layer separated and dried over anhydrous sodium sulphate. The ether having been expelled, the residual liquid was distilled under 50 mm. pressure, 70 g. of ester being thus obtained. It was purified by several redistillations [Found: P, 11·9. $(C_4H_9)_3PO_4$ requires P, 11·7%]. *Tri*-n-*amyl orthophosphate* was prepared in a similar way [Found: P, 10·0. $(C_5H_{11})_3PO_4$ requires P, 10·1%].

The determination of phosphorus in these esters was effected gravimetrically by oxidation with a mixture of concentrated nitric and sulphuric acids, neutralisation with ammonia, and precipitation with ammonium molybdate.

On being distilled, even under 5 mm. pressure in the absence of air, tri-β-methylbutyl, tri-γ-methylbutyl, and tri-*n*-hexyl orthophosphates decomposed, whilst the tri-*n*-amyl ester gave distinct

indications of decomposition on being distilled under 150 mm., and, similarly, tri-*n*-butyl phosphate under 760 mm.

The lower trialkyl orthophosphates, with the exception of the methyl and ethyl members, are incompletely miscible with water at the ordinary temperature, but they mix in all proportions with alcohol, ether, or benzene. The methyl ester possesses a buttery smell, the ethyl a sharp apple-like one, whilst the propyl, butyl, and amyl esters have musty, but pleasant, odours. The *n*-butyl and *n*-amyl phosphates were very slightly yellowish, the colour apparently indicating incipient decomposition.

The boiling points under 50 mm., 100 mm., and 150 mm. were determined in an apparatus which permitted of the constant maintenance of any low pressure by means of a controllable air-leak into a reservoir in conjunction with a " Hyvac " air-pump. Thermometers and barometers standardised at the National Physical Laboratory were employed, and all necessary corrections were applied. In the determinations of density, weighings were corrected for displacement of air. The coefficients of thermal expansion, α, have been calculated by means of the formula,

$$\alpha = (d_{4^\circ}^{25^\circ} - d_{4^\circ}^{40^\circ})/(40d_{4^\circ}^{40^\circ} - 25d_{4^\circ}^{25^\circ}).$$

TABLE I.

Boiling Points, Densities, and Coefficients of Thermal Expansion of Trialkyl Orthophosphates.

Phos-	B.p. under given pressure (mm.Hg).							
phate.	10	50	100	150	760	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{40^\circ}$.	$\alpha \times 10^5$.
Methyl	73°	110°	129°	142°	196°	1·2052	1·1872	104
Ethyl	90	128	148	159	215	1·0637	1·0490	96
n-Propyl	121	161	180	193	252	1·0023	0·9884	96
n-Butyl	150	196	211	227	289	0·9727	0·9596	93
*iso*Butyl	138	177	196	209	264	0·9617	0·9483	96
n-Amyl	—	225	—	—	—	0·9497	0·9373	90

When plotted against temperature, the present values of the density of the methyl ester agree with those of Weger (*Annalen*, 1883, **221**, 89) at 0° and of Cavalier (*Bull. Soc. chim.*, 1898, **19**, 887; *Ann. Chim. Phys.*, 1899, **18**, 460) at 15°, but not with the values given by Arbusov (*J. Russ. Phys. Chem. Soc.*, 1907, **38**, 161) and by Drushel (*Amer. J. Sci.*, 1915, **40**, 643). Similarly, in the case of the ethyl ester the present values are in fair agreement with those given by Zecchini (*Gazzetta*, 1894, **24**, 34) for 28·1°, by Arbusov for 19°, by Arbusov and Ivanov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2015) for 20°, and by Sugden, Reed, and Wilkins (J., 1925, **127**, 1538) for 15° and 38°, but not with those of Cavalier and of Limpricht (*Annalen*, 1865, **134**, 347). The present results accord fairly well

with those of Arbusov and of Drushel for tri-*n*-propyl phosphate, and of Drushel for tri*iso*butyl phosphate at 22°.

In the series of normal phosphates, the average increase in molecular volume from one member to its next homologue is 17·4 c.c. per CH_2 group at 25°, and 17·7 c.c. at 40°. It is noteworthy that at 25° the average difference for a CH_2 group in the case of the lower fatty esters is also *ca.* 17·4 c.c., and at 40° *ca.* 17·5 c.c.

Throughout the range of pressure, p, from 10 mm. to 760 mm., the value of the boiling point, $t°$, given by the following equations agrees within an average error of 0·6° with our direct observations :

Methyl ester :	$8{\cdot}1440 - \log_{10} p = 2468{\cdot}4/(t + 273)$
Ethyl ester :	$8{\cdot}3283 - \log_{10} p = 2658{\cdot}4/(t + 273)$
n-Propyl ester :	$8{\cdot}5188 - \log_{10} p = 2960{\cdot}0/(t + 273)$
n-Butyl ester :	$8{\cdot}5861 - \log_{10} p = 3206{\cdot}5/(t + 273)$
*iso*Butyl ester :	$8{\cdot}9945 - \log_{10} p = 3283{\cdot}1/(t + 273)$

The boiling points under 10 mm. given in Table I have been calculated with these equations, and agree well with the direct measurements of Arbusov (*Ber.*, 1905, **38**, 1172) for trimethyl, tri-*n*-propyl and tri*iso*butyl phosphates under this pressure. Further, the data of Drushel for the last two esters at 15 mm., and of Sugden, Reed, and Wilkins for the triethyl compound at 25 mm., are confirmed by the above equations, but all the boiling points given by Cavalier are too low.

The corresponding values of the molar latent heat of vaporisation are as follows : Trimethyl phosphate, 11,300 cals.; triethyl, 12,170 cals.; tri-*n*-propyl, 13,550 cals.; tri-*n*-butyl, 14,680 cals.; tri*iso*butyl, 15,030 cals.

The refractive indices were measured with a Pulfrich refractometer, made by Wolz of Bonn, and an Abbé refractometer, by Hilger of London. Both instruments were standardised by the use of water and of benzene.

TABLE II.

Refractive Indices of Trialkyl Orthophosphates.

Phosphate.	$n_F^{25°}$.	$n_D^{25°}$.	$n_C^{25°}$.
Methyl	1·3990	1·3950	1·3934
Ethyl	1·4082	1·4039	1·4021
n-Propyl	1·4182	1·4136	1·4118
n-Butyl	1·4274	1·4224	1·4203
*iso*Butyl	1·4222	1·4173	1·4152
n-Amyl	1·4332	1·4283	1·4262

Previous investigators (Zecchini, *loc. cit.*; Arbusov and Ivanov, *loc. cit.*) have measured the refractive index of triethyl phosphate only; it is noteworthy that, on plotting their values for n_D and the present one against temperature, the points obtained all lie on a straight line. Further, the values of n_F and n_C for triethyl phosphate

given by Arbusov and Ivanov agree excellently with those found in the present work.

Owing to the circumstance that the values of the atomic refractivities of oxygen bound to phosphorus are unknown, it is impossible to calculate the atomic refractivity of phosphorus from the values of the molecular refractivities of the phosphoric esters. If it could be assumed that oxygen in an alkyloxy-group possessed the same refractivity as in an ether, use could be made of Lorentz–Lorenz refractivities, *e.g.*, those of Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585), to calculate the value of the refractivity of the orthophosphoryl group, $OP\dot{:}$. However, it appears preferable to derive a value for the refractivity of the orthophosphoric group, $OP(O\cdot)_3$, by deducting the values for carbon and hydrogen from the molecular refractivity of the ester. Values of the refractivity for this group so obtained are given in Table III, where they are denoted by the symbol $[r_L]$, values of molecular refractivity, $(n^2 - 1)M/(n^2 + 2)d$, being denoted by $[R_L]$.

TABLE III.

Molecular and Group Refractivities.

Trialkyl phosphate.	$[R_L]_F$.	$[R_L]_D$.	$[R_L]_C$.	$[r_L]_F$.	$[r_L]_D$.	$[r_L]_C$.
Methyl	28·119	27·869	27·769	10·770	10·715	10·702
Ethyl	42·263	41·870	41·706	10·910	10·862	10·848
n-Propyl	56·394	55·849	55·635	11·037	10·987	10·986
n-Butyl	70·336	69·616	69·312	10·975	10·900	10·872
*iso*Butyl	70·383	69·666	69·358	11·022	10·950	10·918
n-Amyl	84·401	83·567	83·209	11·036	10·997	10·978
			Mean for PO_4	10·958	10·902	10·884

It is hoped that work, now in progress, on the optical properties of alkyl phosphites and of related compounds will help to elucidate the problem of the evaluation of the atomic refractivity of phosphorus when bound to oxygen.

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