121. *Physical Properties of the Lower Dialkyl Hydrogen Phosphites.*

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The vapour pressures and latent heats of dimethyl, diethyl, di-*n*-propyl and di-*n*-butyl hydrogen phosphites have been measured over a wide range of temperature. Cryoscopic measurements both in benzene and in camphor have been carried out. The results suggest that the dimethyl, and to a lesser extent, the diethyl ester are associated in the liquid phase. Higher members of the series, however, are monomeric.

Although dialkyl phosphites have recently become increasingly important as organic intermediates, there is very little information about their physical properties in the literature. For a long time the chief interest lay in their constitution and the valency of the phosphorus atom. More recently, there has been considerable discussion, notably between the schools of Arbuzov and Kosolapoff, as to whether these substances were dimeric in the liquid phase. We have determined the vapour pressures and studied relatively dilute solutions of the lower members of the series cryoscopically in benzene and camphor, and conclude that dimerization, although occurring in dimethyl and diethyl phosphites, is not as important as has been suggested.

Experimental and Results.

Vapour Pressures.—The vapour pressures of dimethyl, diethyl, di-*n*-propyl and di-*n*-butyl hydrogen phosphites were determined by conventional manometry. The manometer and bulb, after being sealed off on a vacuum line, were completely immersed in a paraffin-oil bath. The pressures observed were corrected for expansion of mercury. The results (Fig. 1) can be represented by the equation

$$\log_{10} p_{\mathrm{mm}} = A - B/T$$

The constants A and B, the latent heat of vaporisation, the computed boiling point at 1 atm., and Trouton's constant are given in the Table. The estimated accuracy of the latent heat is ±0·1 kcal./mole and that of the boiling points ±2°.

Hydrogen phosphite	A	B	Latent heat (kcal./mole)	B. p.	Trouton's constant
Dimethyl	7·439	2·0226	9·25	170·6°	20·8
Diethyl	7·174	1·9885	9·10	190·0	19·6
Di-*n*-propyl	7·062	1·9911	9·11	203·0	19·1
Di-*n*-butyl	6·800	1·9732	9·03	230·3	17·9

Samples were obtained from two sources. Dimethyl and diethyl hydrogen phosphites supplied by Messrs. Albright and Wilson were redistilled under vacuum and samples of the diethyl, di-*n*-propyl, and di-*n*-butyl esters were kindly supplied by Dr. V. M. Clark. The agreement between the results obtained with the two specimens of diethyl hydrogen phosphite was satisfactory. Infrared analysis, carried out by Dr. Clark, showed that even after redistillation there were still residual traces of free alcohol.

Cryoscopy.—The freezing points of a series of solutions of the phosphites in benzene were determined in a conventional Beckmann apparatus. The accuracy required to demonstrate the presence of dimerised molecules was well within that of the technique without special precautions. A further series of experiments was carried out with camphor as solvent. The melting points of the solutions were measured on a heated-stage microscope. The results of these two series of experiments are shown in Figs. 2 and 3, where the depression of freezing point, ΔT, is plotted against the mole fraction of solute computed from the monomeric molecular weight.

DISCUSSION

Data relating to the vapour pressures and boiling points are few, being restricted almost entirely to observations of the conditions of distillation, and refer to pressures of the order of magnitude of 1 cm. of mercury. The isolated observations of the boiling point at 1 atm. are in reasonable agreement with those presented here; for example, the normal boiling point of the diethyl ester is given[1] as 186·7°.

The unexpectedly low latent heats suggest that dimerization may occur in the vapour phase. Consequently, we tried to measure the vapour density of the dimethyl ester by Dumas's method, but the experimental difficulties precluded a definite answer. The measured value was consistent with a monomeric form. However, this finding can only be taken to show that, 30° above the normal boiling point, the extent of dimerization is not great.

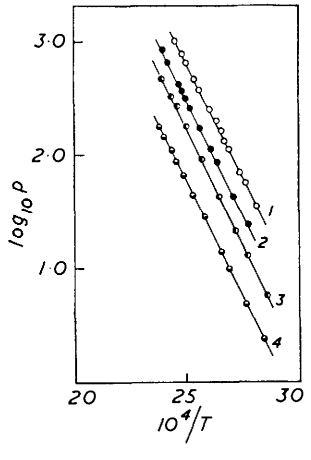

FIG. 1. *Vapour pressures.*

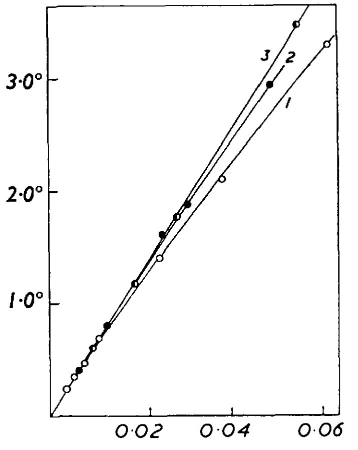

FIG. 2. *Freezing-point depression in benzene.*

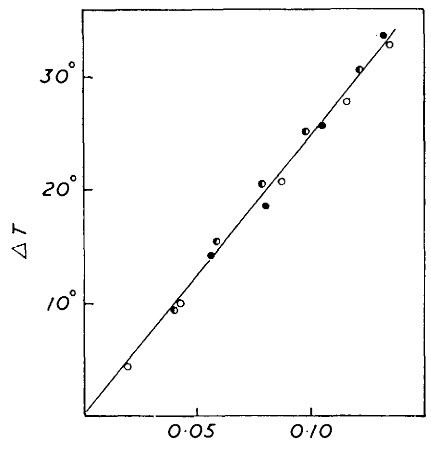

FIG. 3. *Freezing-point depression in camphor.*

Key for all Figs.—1, ○ Dimethyl, 2, ● diethyl, 3, ◐ di-*n*-propyl, 4, ◒ di-*n*-butyl hydrogen phosphite.

One of the easier methods of detection of hydrogen bonding would be a study of the infrared spectra. However, what results have been thus obtained are in conflict. Meyrick

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[1] A. E. Arbuzov, *Ber.*, 1905, **38**, 1171.

and Thompson[2] find evidence for association in the liquid phase while Bellamy and Beecher[3] do not. Arbuzov, Batuev, and Vinogradova[4] obtained evidence from the Raman spectra which supported the view that there was considerable dimerization. Arbuzov and Vinogradova[5] measured the parachors of the dialkyl hydrogen phosphites and claimed to demonstrate dimerization in members of the series as high as dioctyl, though later[6] they modified this statement by suggesting that members above dipentyl were largely monomeric. They supported this by cryoscopy in benzene, which apparently showed that dimethyl hydrogen phosphite, for example, was monomeric only in highly dilute solution. This view was contradicted by Kosolapoff and Powell who studied freezing points in naphthalene[7] and benzene solutions,[8] claiming to demonstrate that the diethyl and di-*n*-butyl esters were monomeric, and that an acidic hydroxyl group was necessary for dimerization. Finally, Arbuzov and Vinogradova,[9] who studied viscosities of solutions in carbon tetrachloride and benzene, suggested that the esters including and above di-*n*-butyl were monomeric, lower members being dimeric.

The cryoscopic evidence now obtained substantiates the general claims of Arbuzov *et al.* that dimethyl and diethyl hydrogen phosphites appear to be partially dimerized in benzene solution. However, Kosolapoff and Powell's measurements are not inconsistent with this. They presented their results as experimental molecular weights without any statement of experimental conditions. These molecular weights were slightly higher than those calculated for the monomeric form. We present our results as the lowering of freezing point, a form which enables divergencies from ideal behaviour to become more apparent. Fig. 2 shows clearly that at mole fractions higher than about 0·02 the dimethyl ester is increasingly associated but the extent of association is only about 13% at mole fraction 0·05. If this result can be extrapolated to 100% of the phosphite this would correspond to about 75% dimerization. The divergence of the diethyl ester from ideality is considerably less and none at all was observed for the di-*n*-propyl in the concentration range examined.

Turning to the measurements at higher temperatures we find that, within experimental error, the freezing-point depression of camphor for all three esters could be represented by a simple straight line when plotted on a mole-fraction basis. This line lay very slightly below the line obtained for naphthalene in camphor but the difference was scarcely more than experimental error and since the difference was common to all the esters it appears to be an activity effect.

We conclude that dimethyl and diethyl hydrogen phosphites are associated at normal temperatures but that the extent of dimerization of the latter is relatively small. Further, there is no evidence of association in solution above about 150° for any of the esters and it is, therefore, unlikely that the vapours should contain significant amounts of dimeric molecules. Thus the low and gradually decreasing Trouton constant with increasing molecular weight probably does not indicate the formation of definite dimers.

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[*Received, August* 26*th*, 1957.]

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[2] Meyrick and Thompson, *J.*, 1950, 225.
[3] Bellamy and Beecher, *J.*, 1952, 475.
[4] A. E. Arbuzov, Batuev, and Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, 1946, **54**, 599.
[5] B. A. Arbuzov and Vinogradova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1947, 459.
[6] *Idem, Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, 695.
[7] Kosolapoff and Powell, *J.*, 1950, 3535.
[8] *Idem, J. Amer. Chem. Soc.*, 1950, **72**, 4291.
[9] B. A. Arbuzov and Vinogradova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1952, 507.