Some Physical Properties of Aliphatic Diphosphonates. Part I. Ethyl Esters.

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A family of esters of the general type $[CH_2]_x[PO(OEt)_2]_2$ was examined from $x = 1$ to $x = 5$ in respect to dielectric constant, index of refraction, density, and viscosity. The values of the dipole moments of these esters, calculated from the above data, showed good agreement with the data obtained previously for the monophosphonates.

As a result of the examination of some physical properties of various dialkyl alkyl-phosphonates, in which the variations of these properties were correlated with structure (Kosolapoff, *J.*, 1954, 3222; 1955, 2964; *J. Amer. Chem. Soc.*, 1954, **76**, 615), it was deemed advisable to examine a series of tetra-alkyl aliphatic diphosphonates, $(RO)_2P(O)\cdot[CH_2]_x\cdot P(O)(OR)_2$, in a similar manner. The tetraethyl esters were selected for the initial work because they are more readily purified than are the higher esters in this series, which boil at considerably higher temperatures. The esters examined were those in which x was 1—5.

The results of the measurements, which are recorded in the Table, showed some interesting points. The density–temperature plots of the five esters showed essentially the same slope, indicating a substantial independence of the degree of separation of the polar groups by the methylene units. The viscosity–temperature plots, however, showed a significant progression of differences. Thus, the esters with $x = 3$, 4, and 5 gave nearly identical viscosity–temperature curves, with a decided increase of the slopes at temperatures below 50°. The esters with $x = 1$ and 2 gave progressively lower viscosity values, indicating a considerable effect of the approach of the two polar groups to each other. Further, the decline in viscosity in the overall interval of temperature from 30° to 70° was much more pronounced for the esters with $x = 3$, 4, or 5 than with $x = 1$ or 2.

The values for the indices of refraction in this group of esters, with the density data, were used for the calculation of the molar refractions. In view of the fact that this had not been done previously with the diphosphonates, it is noteworthy that the value of 4·27 for the " phosphonate " type of phosphorus appears to apply very well indeed to the diphosphonates, as it does to the monophosphonates.

The values of the dielectric constants in this series, as expected, show a rise with the decreased separation of the polar groups by the methylene groups. The only relative anomaly is the high value found for the compound with $x = 3$, which is somewhat greater than that for the ester with $x = 2$.

From the data listed above it was possible to compute the dipole moments of the substances with the use of Onsager's equation (cf. Kosolapoff, *loc. cit.*). Owing to the structural complications in this family of esters, the use of Buckingham and Le Fèvre's formula (*J.*, 1952, 1932) was not feasible. The calculated dipole moments (see Table) were closely grouped, ranging only from 4·23 D for the methylene member to 4·38 D for the trimethylene member, the latter again being anomalous. The complete identity of the dipole moments for the esters with $x = 4$ and 5 is to be expected, possibilities of unrestricted rotation being common to both. The dipole moment of the methylene member was of a special interest. This value, 4·23 D, affords an independent check on the dipole-moment values calculated for the monophosphonates, particularly that for diethyl methylphosphonate. The latter, as reported earlier (Kosolapoff, *loc. cit.*), was found to be 3·33 D when calculated by Onsager's formula, or 3·11 D as the root-mean-square value of the two values (2·82 and 3·39 D, respectively) calculated, for the two extreme rotational possibilities of the side chains, by the Buckingham–Le Fèvre formula. If a not unreasonable assumption is made that the valency angle at the methylene group of the diphosphonate is close to the tetrahedral value, the calculated dipole moment of the diethyl phosphono-group is then equal to 4·23/1·15, or 3·68 D. With allowance for the polarity of the C–H link, necessary for such comparison, and equal probably to 0·3—0·4 D, the value of the moment of the polar part of the molecule agrees very well with the dipole moment of diethyl methylphosphonate as calculated by Onsager's equation, thus further justifying the use of this formula (and data obtained on the dielectric constant of pure liquids, as contrasted to solutions) for the esters of phosphorus acids. The rotational possibilities for the higher members in this family make any preliminary computations from their individual dipole moments unjustifiable.

EXPERIMENTAL

Preparation of Esters.—The esters were prepared by the conventional reaction of the organic dihalides with triethyl phosphite. When a 50% excess of triethyl phosphite was used over the calculated amount of 2 moles per mole of the dihalide, satisfactory yields of the diphosphonates were obtained, except in the case of the methylene member, as expected. The yields and the b. p.s of the esters are listed below :

x	1	2	3	4	5
B. p./mm.	127°/0·5	152°/0·5	163°/1	169°/0·7	178°/0·6
Yield (%)	26	61	72·5	61·6	62·3

It was intended originally to supplement this series by the corresponding tetra*iso*propyl esters. However, it was found that while tri*iso*propyl phosphite gives a generally better yield of the desired products, owing to the elimination of the side-reaction of formation of the phosphonate, $RP(O)(OR)_2$, the ethylene member of the series, $(Pr^iO)_2P(O) \cdot CH_2 \cdot CH_2 \cdot P(O)(OPr^i)_2$, was a rather high-melting solid (m. p. 52—53°); this unexpected result thus produced a gap in the proposed series, since the solid substance would not be suitable for the determination of dielectric constant and viscosity (at least below the m. p.). Incidentally, this ester is rather hygroscopic, becoming liquid after a short exposure to the air; a brief evacuation with a good pump at moderate temperature restores the solid state readily. In view of the above anomaly, physical measurements on this group of *iso*propyl esters were abandoned.

The dihalides employed in the preparations were the bromides, except for the methylene compound, which was the iodide. Tetramethylene bromide was prepared by hydrolytic cleavage of tetrahydrofuran by heating it with 48% hydrobromic acid–sulphuric acid; this

afforded a very clean reaction which in 1 hr. gave a 90·5% yield of the dibromide in one run and a 93% yield in another. The method often used for this preparation, *viz.*, reaction with dry hydrogen bromide, is relatively slow and produces much tar. Pentamethylene bromide was prepared similarly from tetrahydropyran in an 89% yield.

Physical constants of esters of type $[CH_2]_x[PO(OEt)_2]_2$.

$x =$	t	d_4^t	η (P)	$x =$	t	d_4^t	η (P)		n_D^{30}	[M_R] found	calc.	ε^{30}	μ (D)
5	30°	1·0880	0·1549	2	30	1·1263	0·1100	$x = 5$	1·4443	84·04	83·97	11·070	4·28
	40	1·0790	0·1048		40	1·1169	0·0771	$x = 4$	1·4442	79·43	79·35	11·635	4·28
	50	1·0707	0·0726		50	1·1078	0·0570	$x = 3$	1·4422	74·77	74·73	12·696	4·38
	60	1·0620	0·0559		60	1·0987	0·0446	$x = 2$	1·4375	70·32	70·12	12·267	4·20
	70	1·0533	0·0433		70	1·0895	0·0338	$x = 1$	1·4261	65·17	65·49	12·768	4·23
4	30	1·1040	0·1548	1	30	1·1325	0·0982						
	40	1·0953	0·1039		40	1·1229	0·0675						
	50	1·0864	0·0724		50	1·1134	0·0497						
	60	1·0778	0·0555		60	1·1039	0·0387						
	70	1·0692	0·0428		70	1·0944	0·0306						
3	30	1·1186	0·1554										
	40	1·1097	0·1030										
	50	1·1008	0·0699										
	60	1·0917	0·0528										
	70	1·0825	0·0412										

The samples for the physical measurements on the diphosphonates were taken from the mid-portions of steadily-boiling specimens, distilled through an efficient ring-packed fractionating column. Freshly distilled specimens were employed.

The dielectric measurements were made as described previously (Kosolapoff, *J.*, 1954, 3222) at 30°. Viscometric determinations were made with the conventional Ostwald viscometer immersed in a thermostatically controlled oil-bath. Density measurements were made with a pyknometer.

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