The number-average molecular weight of this sample was not measured, but we expect a value not much over 1,000,000, since the polymer was made under conditions where the chain termination was diffusion controlled.23 We have shown before¹⁰ that such polymers have broad molecular weight distributions. The intercept of the high angle asymptote of sample 10 corresponds to a number-average molecular weight of nearly 3,000,000, however.

A more severely curved Zimm plot (Fig. 8) was obtained from a sample with a very broad molecular weight distribution made by mixing 1 part of sample 10 and 10 parts of sample 3. The observed weight-average molecular weight of the mixture agrees well with the calculated value of just over 1,000,000.

The number-average molecular weight of the mixture is essentially the same as that of sample 3, or about 130,000. The high angle asymptote gives $\bar{M}_{n} = 170,000.$

The value of \bar{r}_n for this sample, from the high angle slope, is 935 Å., identical with the size found

(23) E. Trommsdorff, H. Kohle and P. Lagally, Makromol. Chem., 1, 69 (1947); G. V. Schulz and G. Harborth, ibid., 1, 104 (1947).



Fig. 8.-Zimm plot of a mixture of polymethyl methacrylate samples 10 (1 part) and 3 (10 parts).

by Bischoff and Desreux for a fraction with a molecular weight of 1,000,000.

The value of $\tilde{r}_z = 3400$ Å, for this sample appears too low, as it should correspond to that found for one of our whole polymers with the same z-average molecular weight as the mixture. We estimate this size to be well over 5,000 Å.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEXAS TECHNOLOGICAL COLLEGE]

Electric Moments of Some Alkyl Phosphates and Thiophosphates

BY GEORGE K. ESTOK AND WESLEY W. WENDLANDT

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Electric moments at 25° in benzene solution have been determined for triethyl- and tri-n-butyl phosphate, and triethyland tri-*n*-butyl thiophosphate. The respective values are 3.08, 3.07, 2.82 and 2.84. From this, and other work, the values of 3.3 ± 0.1 and 3.0 ± 0.1 have been assigned as the most probable bond moments for the P \rightarrow O and P \rightarrow S semi-polar Dielectric constants were also determined for liquid tri-n-butyl phosphate (8.05 ± 0.05) and tri-nbonds, respectively. butyl thiophosphate (6.82 \pm 0.03), and the respective moments calculated by Onsager's equation are 3.35 and 3.02.

Disagreements have been noted in the literature relative to assigned values for the bond moments of the semi-polar $P \rightarrow S$ and $P \rightarrow O$ bonds in certain compounds. From electric moment determinations of thiophosphoryl chloride (PSCl₃) and phosphorus oxychloride (POCl₃),¹ and triphenyl thiophosphate and triphenyl phosphate,² Smyth and co-workers arrived at values of 2.5 and 3.2 D, respectively, for the $P \rightarrow S$ bond moments in PSCl₃ and triphenyl thiophosphate, and 3.5 D for the $P \rightarrow O$ bond moments in both the oxychloride and the phosphate. The low value of 2.5 for the $P \rightarrow S$ moment in PSCl₃ is reasonably attributed to the easy polarization of the sulfur atom by the highly electronegative chlorine atoms. Arbuzov and Shavsha³ worked with alkyl thiophosphates which led them to assign what seems an abnormally high value of 3.55 D for the P \rightarrow S bond moment. Arbuzov and Rakov⁴ worked with alkyl phosphates, and in this case were in agreement with Smyth by assigning 3.5 for the $P \rightarrow O$ moment.

Svirbely and Lander,⁵ from a moment determina-(1) C. P. Smyth, G. L. Lewis, A. J. Grossman and F. B. Jennings,

THIS JOURNAL, 62, 1219 (1940).

- (3) B. A. Arbuzov and T. G. Shavsha, C. A., 46, 3817d (1952). (4) A. E. Arbuzov and P. I. Rakov, ibid., 44, 8713g (1950).
- (5) W. J. Svirbely and J. J. Lander, THIS JOURNAL, 70, 4121 (1948).

tion on triethyl phosphate chose a value of 2.8 for the P \rightarrow O moment, a value also suggested by Lister and Sutton⁶ on the basis of unpublished work by a colleague (J. S. Hunter). Recalculations⁷ on the method of Svirbely and Lander (hereinafter called Method II) indicate that 2.7 would derive from their treatment instead of 2.8 as published. If 1.2 for the P-O covalent link moment (from work of Lewis and Smyth, hereinafter called Method I) is used, instead of 1.4, then the semipolar $P \rightarrow O$ moment calculates to be 2.5 by Method II. Thus, depending on method and assumptions used, values ranging from 2.5 to 3.5 have been calculated for the $P \rightarrow O$ bond moment.

The experimental work and analysis reported here were undertaken to help clarify the above mentioned situation, particularly in view of the fact that the moments previously reported³ for certain alkyl thiophosphates appeared anomalous.

Experimental

Triethyl phosphate, an Eastman Kodak Co. yellow label product, was carefully fractionated at reduced pressure

⁽²⁾ G. L. Lewis and C. P. Smyth, ibid., 62, 1529 (1940).

⁽⁶⁾ M. W. Lister and L. E. Sutton, Trans. Faraday Soc., 35, 495 (1939).

⁽⁷⁾ Dr. Svirbely advises by private communication that errors in calculation occurred in connection with use of his equations 7, 6, and 1, in reference 5.

SLOPE-INTERCEPT DATA, POLARIZATIONS AND ELECTRIC MOMENTS (25°)

	$\Delta(\Delta \epsilon/m_2)$		$\Lambda(\Lambda d/m)$					
Solute	Δw_2	$(\Delta \epsilon / w_2)_{\infty}$	Δw_2	$(\Delta d/w_2)_{\infty}$	$P_{2\infty}$	MRD	(benzene)	(Ons
(EtO) ₃ PO	4.5	5.47	0.012	0.161	238.4	41.8	3.08	
(n-BuO) ₃ PO	2.4	3.68	.012	.091	266.0	69.6	3.07	3.
(EtO) ₃ PS	3.6	4.27	.003	. 164	214.5	49.5	2.82	
(n-BuO) ₃ PS	2.2	3.02	.011	.096	246.4	77.1	2.84	3.

through a glass helix packed column; b.p. 204° (680 mm.), 130° (55 mm.), n^{25} D 1.4034, d^{25} 4 1.0643.

¹³⁰ (55 mm.), n^{25} D 1.4034, d^{25}_{4} 1.0643. **Tri-n-butyl phosphate**, an Eastman Kodak Co. white label product, was similarly purified; b.p. 160° (15 mm.), n^{25} D 1.4223, d^{25}_{4} 0.9726, ϵ^{25} 8.05 ± 0.05. **Triethyl thiophosphate**, b.p. 104° (17 mm.), n^{25} D 1.4462, d^{25}_{4} 1.0684, and **tri-n-butyl thiophosphate**, b.p. 166° (19 mm.), n^{25} D 1.4492, d^{25}_{4} 0.9816, ϵ^{25} 6.82 ± 0.03, were pro-rided but the constraint of Usinging Charling Charling 100 mm. vided by the courtesy of Virginia-Caroline Chemical Corp., Richmond, Va., and were purified by fractionation at reduced pressure.

Benzene solvent, ϵ^{25} 2.273, d^{25}_4 0.8726, was purified as previously indicated.⁸

Measurements and Calculations .- Work in benzene solution was done as previously described⁹ using the method of Hedestrand as modified by LeFevre and Vine.¹⁰ For the dielectric constants of the pure liquids a cell similar to the solution cell was used, except that it had an electrical capacity of 50 mmf.

Molar refractions were calculated from the densities and refractive indices of the purified liquids. **Moments** in solution were calculated from the relation: $\mu = 0.221 (P_{2\infty})$ $1.05 MRD)^{1/2}$. Moments based on the liquids were calculated from the Onsager equation¹¹

$$\mu^2 = \frac{M}{d} \times \frac{9kT}{4\pi N} \times \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2}$$

where N is Avogadro's number (as compared to Onsager's molecules/cm.3).

Discussion of Results

The moments of alkyl thiophosphates reported by Arbuzov and Shavsha³ scatter between values of 2.91 and 3.18, and the average of 3.06 is also about the average value for alkyl phosphates. The thiophosphates, however, would be expected to have somewhat lower moments than the phosphates. Thus Lewis and Smyth² report 2.81 and 2.58 for triphenyl phosphate and thiophosphate, respectively. Values reported here in Table I show 3.08 and 3.07 for triethyl- and tri-n-butyl phosphate, and 2.82 and 2.84 for the corresponding thiophosphates, whereas Arbuzov has reported 2.91 and 3.04 for the latter pair. Moment values (On-



Fig. 1.—Relative diminution (A), and augmentation (B), of the effect of the primary $P \rightarrow O$ (or $P \rightarrow S$) bond moment due to extreme orientations.

02sager) in Table I also show the thiophosphate to be lower in moment. Thus the high value of 3.55 assigned by Arbuzov for the $P \rightarrow S$ bond moment appears to be the result of using a too high average

moment for alkyl thiophosphates. The question of assigning a high value of about 3.2-3.5 (Method I) or a low value of about 2.5-2.7(Method II) for the semi-polar $P \rightarrow O$ bond moment involves opposite viewpoints as to the role of the $(RO)_{3}P$ portion of the phosphate (or thiophosphate) molecule. The value 3.5 is greater than the total phosphate moment, whence in Method I the (RO)₃P portion is considered to act in a sense opposite to the $P \rightarrow O$ moment. The value 2.7 is less than the total moment of an alkyl phosphate, and thus in method II the (RO)₃P portion is considered to augment the primary $P \rightarrow O$ moment.

Examination of scale models reveals that of all the orientations of the rotating groups, those which act in a sense opposite to the primary $P \rightarrow O$ (or $P \rightarrow S$) bond moment do so more strongly than the orientations which augment the primary moment. This is illustrated in Fig. 1. It would thus appear that the semi-polar bond moment should be larger than the total moment for the molecule.

In Method I the values 3.5 and 3.2 for $\mathrm{P} \rightarrow \mathrm{O}$ and $P \rightarrow S$ were calculated assuming C-O-P, O-P-O and $O-P \rightarrow O$ (or $O-P \rightarrow S$) angles of 110, 100 and 118°, respectively, in analogy to the phosphite molecule. Additional calculations were also made, however, assuming all angles to be 110° , in which event the values 3.2 and 2.9 resulted, but these were considered less probable. In Method II all bond angles were assumed to be 110°.

In view of the fact that the bond angles Cl-P-Cl in PCl₃ have been measured as 101°, and in POCl₃ near 106° , 1^2 it appears reasonable to assume tetra-hedral angles of 109.5° , due to some additional spreading of the O–P–O angles, in the phosphates and thiophosphates. In this case the values 3.2 and 2.9 for $P \rightarrow O$ and $P \rightarrow S$ would seem preferable.

Further examination, however, of models of the triphenyl esters indicates that steric effects hinder considerably those extreme orientations which tend to augment the primary moment. No significant hindrance occurs in those orientations which diminish the influence of the $P \rightarrow O$ linkage. Thus the triphenyl esters have moments which are less than those for the alkyl analogs. If free rotation were possible the moments of the triphenyl phosphate and thiophosphate would be more nearly equal to those of the alkyl phosphates and thiophosphates, respectively. Thus the values for the $P \rightarrow O$ and $P \rightarrow S$ moments could reasonably be somewhat higher than 3.2 and 2.9, and probably within the

ager)

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⁽⁸⁾ J. Moede and C. Curran, THIS JOURNAL, 71, 852 (1949).

⁽⁹⁾ G. K. Estok and J. H. Sikes, ibid., 75, 2745 (1953).

⁽¹⁰⁾ R. J. W. LeFevre and H. Vine, J. Chem. Soc., 1805 (1937).

⁽¹¹⁾ L. Onsager, THIS JOURNAL, 58, 1490 (1936).

⁽¹²⁾ L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca. N. Y., 1945, pp. 80-84.

limits 3.3–3.4 and 3.0–3.1, respectively. These values are consistent with those obtained from the data in Table I through use of Smyth's equations, as indicated in the following paragraph.

Assuming all tetrahedral angles of 109.5° the equations of Lewis and Smyth² may be rearranged into the following quadratic form most suitable for algebraic substitution

 $m_3^2 + 6\cos\theta \left[(m_2 + m_1\cos\theta)m_3 + m_2(m_1 + m_2) + m_1\cos\theta(m_1\cos\theta + 2m_2) \right] + 3(m_1^2 + m_2^2) - \mu^2 = 0$

Here m_3 is the P \rightarrow O (or P \rightarrow S) bond moment, m_1 the C-O moment, m_2 the covalent P-O moment, cos θ is -0.334, and μ is the total moment determined in benzene solution. Using $m_1 = 1.1$, $m_2 = 1.2$, and the appropriate average moments of 3.08 and 2.83 from Table I, the values 3.3 and 3.0 are obtained for the P \rightarrow O and P \rightarrow S bond moments, respectively.

The value of 3.5 assigned by Smyth¹ for the $P \rightarrow O$ moment in POCl₃ is based on the addition of the POCl₃ moment (2.4) and a value of 1.1 for the PCl₃ moment, the origin of this latter value being ob-

scure. If a P-Cl bond moment of 0.81 (based on 1.1 for PCl₃) is used, and correction made for angles of 106° in POCl₃,¹² then the P \rightarrow O moment calculates about 3.35 D. If the literature value of 0.90 for PCl₃ in benzene solution¹³ is accepted and added to 2.4 for POCl₃, the value 3.3 is obtained for P \rightarrow O. The slight additional correction for Cl-P-Cl widening to 106° lowers the value to about 3.15 D. This slightly lower value than 3.3 is easily attributable to a slight polarization of the oxygen atom by the chlorine atoms in a manner similar to that which produced a strong inductive effect on the sulfur atom.

Although an analysis of the nature reported here is necessarily approximate, it appears that 3.3 ± 0.1 and 3.0 ± 0.1 are optimum values for the P \rightarrow O and P \rightarrow S semi-polar bond moments, respectively, when these bonds are not appreciably influenced by induction.

(13) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Mass. Inst. of Technology, Cambridge, Mass., 1948.

LUBBOCK, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEXAS TECHNOLOGICAL COLLEGE]

Electric Moments of Some Unsaturated Carbonyl Compounds¹

By George K. Estok and John S. Dehn Received March 21, 1955

Electric moments have been determined in benzene and dioxane solution for a number of unsaturated methyl ketones and aldehydes having moments in the range 3.20 to 3.58 D. The results are interpreted in terms of resonance, preferred configurations and solvent effects. Analysis of this and previous work indicates that aliphatic unsaturated aldehydes, and β -disubstituted ketones, have predominantly the s-trans, and s-cis configurations, respectively. The β -monosubstituted unsaturated ketones appear to have approximately equal contributions from both the s-trans and s-cis configurations.

This work may be considered as part two of work previously reported² relative to preferred configurations in unsaturated methyl ketones having moments below 3.0 D. Results are now reported on molecules having moments greater than 3.0 D, with further structural analysis.

Experimental

Preparation and Purification of Compounds.—Boiling points, unless otherwise indicated, have been corrected to 760 mm.

Crotonaldehyde, a Matheson Co. product, was carefully dried and fractionated just prior to use; b.p. 102° , $n^{25}D$ 1.4342, d^{25}_{4} 0.848.

Ethylideneacetone was prepared by an aldol type condensation in which acetone and acetaldehyde were condensed with dilute NaOH as catalyst.³ It was purified by careful fractionation at reduced pressure; b.p. 122-123°, n^{25} D 1.4333, d^{25} , 0.8592.

 α -Methylethylidene acetone was prepared by a condensation of acetaldehyde and ethyl methyl ketone at -10° , using dry HCl as catalyst.⁴ The product was twice fractionated at reduced pressure; b.p. 138°, b.p. 63° (49 mm.), n^{25} p 1.4469, d^{25} , 0.8697.

Benzylideneacetone, an Eastman Kodak Co. white label product, was recrystallized twice from ligroin; m.p. 40°. Methyl *p*-tolyl ketone, an Eastman Kodak Co. white

Methyl *p*-tolyl ketone, an Eastman Kodak Co. white label product was carefully fractionated twice at reduced pressure; b.p. 116° (26 mm.), n^{25} D 1.5313, d^{25} , 0.999.

(1) Presented at the 10th Southwest Regional Meeting of the American Chemical Society, Forth Worth, Texas. December 2-4, 1954.

p-Tolualdehyde, an Aldrich Chemical Co. research grade material, was used without further purification; b.p. 204°, n^{25} D 1.5432, d^{25} , 1.0155.

Benzene and dioxane were purified as indicated in earlier work.²

Measurements and Calculations.—The general procedure was as indicated in earlier work.² Moments were calculated from the equation

 $\mu = 0.2208 (P_{2\infty} - 1.05 MRD)^{1/2}$

Molar refractions for liquids were calculated from densities and refractive indices; for benzylideneacetone atomic refractions were used with an estimate for a slight exaltation.

Discussion of Results

Table I lists the pertinent data relating to the moments which have been determined. Configurational results based on this and previous work^{2,5,6} are indicated in Table II.

Data for β -methylcrotonaldehyde and α,β -dimethylcrotonaldehyde have been estimated. The s-trans configuration is indicated for all the aldehydes (except p-tolualdehyde, whose two preferred configurations are equivalent). Ketones with residues of three or less carbon atoms as anchorage for the carbonyl group also appear to be predominantly s-trans. The s-cis configuration is indicated for mesityl- and methylmesityl oxides, in which steric hindrance occurs between the carbonyl

(5) J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton. *ibid.*, 2957 (1949).

⁽²⁾ G. K. Estok and J. H. Sikes, THIS JOURNAL, 75, 2745 (1953).

⁽³⁾ V. Grignard and M. Fluchaire, Ann. Chim., 9, 10 (1928).

⁽⁴⁾ L. E. Hinkel, J. Chem. Soc., 817 (1931).

⁽⁶⁾ L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Mass. Inst. of Technology, Cambridge, Mass., 1948.