The first fractions were composed of pure 1-methyl-1-phenylvinyl bromide (II), while the end fractions were composed of 2-phenylallyl bromide (I); about 24% of I underwent polymerization during separation. From the infrared spectra of the pure I and II isomer it was calculated that the crude bromides were composed of 73% of I and 27% of II.

Compound I: b. p. 104–105° at 10 mm., n_D^{20} 1.5925, d_4^{20} 1.3729. MR_D: found 48.39; calcd. 47.46. λ_{max}. 242 mμ.: ε 8,700 (in isooctane).

Anal. Calcd. for C_9H_9Br: C, 54.82; H, 4.57. Found: C, 54.90; H, 4.49.

Compound II: b.p. 98° at 10 mm., n_D^{20} 1.5891, d_4^{20} 1.3716. MR_D: found 48.39, calcd. 47.46. λ_{max}. 247 mμ (in isooctane) ε 13,240 (in isooctane) Literature:[7] b.p. 105–106° at 9 mm., d_4° 1.366.

Anal. Calcd. for C_9H_9Br: C, 54.82; H, 4.57, Found: C, 54 78; H, 4.44.

Ozonolysis of II. Compound II, 2.35 g., dissolved in 25 ml. of methylene chloride was ozonized at −78°. The ozonide was decomposed by the usual method with hot water. Acetophenone, 1.23 g., (89%) was obtained which formed 2,4-dinitrophenylhydrazone, m.p. 246°. It did not depress the melting point of an authentic sample.

Synthesis of 2-phenyl-1,5-hexadiene. Phenylallyl bromide, I, 31 g. was reacted with 15% excess of allylmagnesium bromide. A 78% yield of 2-phenyl-1,5-hexadiene was obtained, which distilled at 104° at 10 mm, n_D^{20} 1.5314.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.75; H, 8.75.

Ozonolysis of 2-phenyl-1,5-hexadiene. Two grams of the hydrocarbon dissolved in 25 ml. of methylene chloride was ozonized at −78° and decomposed oxidatively,[8] except that no sulfuric acid was added. The benzoylpropionic acid which was obtained melted, after recrystallization from water, at 116–117° (literature[9]) m.p. 116.5°.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.41; H, 5.62. Found: C, 67.11; H, 5.95.

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Effect of Substituents on the Rates of Pyrophosphate Hydrolysis[1]

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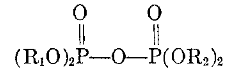
In a recent paper,[2] Heath has summarized (from earlier work of Ketelaar and Blaksma,[3] and of Toy[4,5]) the neutral hydrolysis rate constants of the pyrophosphates listed below. Since Heath has concluded that the transmission of electronic effects along the P-O-P bond is small,[6] the observed rate constant will be the sum of the rate constants for the groups attached to each phosphorus atom. Individual rate constants were obtained based upon the symmetrical pyrophosphates. Using these constants to calculate the expected rate for the unsymmetrical pyrophosphates, agreement was observed only in the cases when R_1 = Et, R_2 = Pr, and R_1 = Et, R_2 = *n*-Bu. Consequently, Heath concluded that steric effects are very much more important than inductive effects in this series.

TABLE I

RATE CONSTANTS FOR HYDROLYSIS OF PYROPHOSPHATES,



$$(R_1O)_2\overset{\overset{\displaystyle O}{\|}}{P}—O—\overset{\overset{\displaystyle O}{\|}}{P}(OR_2)_2$$

No.	R_1	R_2	$k \times 10^3$ min^{-1}	$\Sigma\sigma^*$
1	Me	Me	25	0.000
2	Me	Et	7.0	−0.200
3	Me	Pr	5.6	−0.230
4	Et	Et	1.6	−0.400
5	Me	iPr	1.1	−0.380
6	Et	nPr	1.0	−0.430
7	Et	nBu	0.95	−0.460
8	nPr	nPr	0.65	−0.460
9	Et	iPr	0.28	−0.580
10	nPr	iPr	0.20	−0.610
11	nBu	iPr	0.20	−0.640
12	iPr	iPr	0.09	−0.760

The hydrolysis data have been reexamined in an attempt to establish a quantitative correlation of these reaction rates with structure.

All of the above data are correlated successfully by means of Taft's linear free energy-polar energy equation.[7]

$$\log k/k_0 = \rho^*\Sigma\sigma^*$$

where ρ^* = reaction rate constant, $\Sigma\sigma^*$ = sum of polar substituent constants (aliphatic series), k = observed rate constant, k_0 = observed rate constant for tetramethyl pyrophosphate. The accompanying figure gives the plot of log k/k_0-vs. $\Sigma\sigma^*$, the line being that calculated using the method of least squares. The following constants were obtained: $\rho^* = 3.38 \pm 0.08$, intercept = 0.0561 ± 0.0376, correlation coefficient = 0.994.

Unfortunately, the range of σ^* values is small. Consequently, if the above correlation is confirmed for the reaction with groups of greater σ^* values, then the following conclusions, based on this limited data, will follow.

1. The fact that the total polar effect of all groups is operative, as given by $\Sigma\sigma^*$, indicates a

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(1) The work herein reported was carried out on Project NR055-328 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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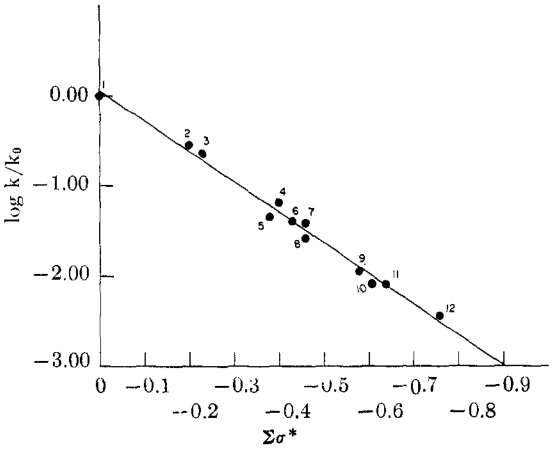
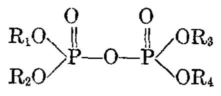


FIG. 1. PLOT OF LOG k/k_0 *vs.* $\Sigma\sigma^*$. Numbers refer to pyrophosphates in Table I.

symmetrical transition state for the P-O-P structure. Possibly the rate-determining step involves an attack on the central oxygen atom, followed by a rapid scission of one of the P-O-P bonds. This postulate is in contrast to the proposed P-O bond scission in phosphate ester hydrolysis as the rate-determining step.[8] A mechanism involving two independent attacks by water molecules on each phosphorus atom, as suggested by Heath[2] is ruled out. The fact that the observed rate constants almost agree in the two cases cited above with the sum of two rate constants calculated from the symmetrical pyrophosphates is purely fortuitous.

2. These reactions are influenced chiefly by polar effects, and very little, if at all, by steric effects, as is strikingly demonstrated by the high value of the correlation coefficient and by the agreement of the rate constant for tetraisopropyl pyrophosphate which obeys the above relationship. This conclusion is in conflict with those of Toy[6] and Heath.[2]

3. In the data available, all pyrophosphates of general structure



have either $R_1{=}R_2{=}R_3{=}R_4$ or $R_1{=}R_2$ and $R_3{=}R_4$. Due to the fact that the correlation depends on $\Sigma\sigma^*$, it is expected that it will also hold when $R_1{=}R_3$, $R_2{=}R_4$ and when $R_1 \neq R_2 \neq R_3 \neq R_4$.

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Preparation of 2-Hydroxydiethyl Sulfoxide[1]

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Many procedures for the preparation of sulfoxides are based on the controlled oxidation of the corresponding sulfides. Difficulties are sometimes encountered with these methods when sulfones are formed, resulting in purification complications, and when other portions of the molecule are attacked by the oxidation process. Both of these difficulties were encountered in attempts to prepare 2-hydroxydiethyl sulfoxide from 2-hydroxydiethyl sulfide by conventional methods.

Patein[2] has shown that the reaction

$$R_2S + Br_2 \longrightarrow R_2SBr_2 \xrightarrow{H_2O} R_2SO + 2HBr$$

quantitatively forms the sulfoxide and hydrobromic acid. This reaction has since been used as a basis for the determination of sulfides[3–5] and by Harnish and Tarbell[5] for the preparation of benzyl phenyl sulfoxide. It has been used on occasion by a few other workers for sulfoxide preparation.[6]

Pure 2-hydroxydiethyl sulfide reacts stochiometrically with bromine when determined by the method of Siggia.[4] It was impractical to separate the sulfoxide from this analytical reaction mixture, and the preparative reaction was carried out by adding pure bromine to the acidified aqueous solution of 2-hydroxydiethyl sulfide. The equivalence point could be observed precisely by the appearance of the yellow bromine color when a slight excess bromine was added. The final reaction mixture contained the sulfoxide, water, hydrobromic acid, and a little hydrochloric acid. 2-Hydroxydiethyl sulfide is soluble in about five parts of water and the sulfoxide is very soluble. The extraction of the sulfoxide from the neutralized and salted reaction mixture with ether was very inefficient because of the unfavorable partitioning. However, it was found that an anion-exchange column (Amberlite IR-4B) retained the acids completely with excellent recovery of the product in dilute aqueous neutral solution. Concentration and distillation gave pure 2-hydroxydiethyl sulfoxide.

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