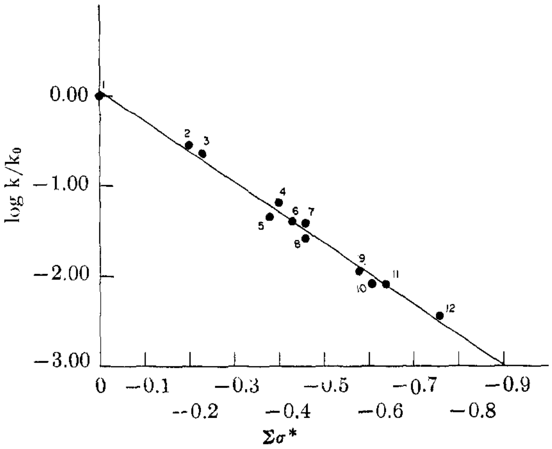
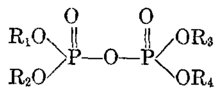


FIG. 1. PLOT OF LOG k/k_0 *vs.* $\Sigma\sigma^*$. Numbers refer to pyrophosphates in Table I.

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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[1] This investigation was supported in part by funds provided for biological and medical research by the State of Washington Initiative Measure No. 171. Scientific Paper No. 1576, Washington Agricultural Experiment Stations. Work conducted under Project No. 1229.

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EXPERIMENTAL

2-Hydroxydiethyl sulfoxide. 2-Hydroxydiethyl sulfide (74.3 g., 0.70 mole) was placed in an 800 ml. beaker containing 225 ml. water and 10 ml. concentrated hydrochloric acid. Bromine was added to the well stirred mixture from a buret having a long capillary tip that extended below the surface of the solution. The rate of addition was regulated so that the bromine reacted as fast as it was added. Water was added at intervals to reduce the hydrobromic acid concentration, until the final volume of the mixture was about 500 ml. Near the equivalence point (indicated by slight persistence of color) the rate of addition of bromine was reduced and the final additions were made dropwise until one drop colored the mixture yellow.

The mixture was diluted to 2000 ml. and passed in two 1000 ml. portions through a column containing about 400 g. moist IR-4B resin. The column was washed with water until a total of 3000 ml. neutral solution had been collected.

The sulfoxide solution was concentrated in a flash vacuum evaporator and the remaining water removed at 60° C. under 10 mm. pressure. The product was finally distilled in a molecular still at 54° C. A yield of 70% was obtained with much of the loss mechanical. Analysis by a modified method of Barnard[7–9] for sulfoxide indicated 100.4 ± 0.7% sulfoxide.

Calcd. for $C_4H_{10}OS$: S, 26.26. Found: S, 26.47.

The product had a density of 1.1685 25°/4°, and a refractive index, n_D^{25} 1.5019. The vapor pressure at 54° C. was estimated from molecular distillation data at about 3 microns.

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Nitric Acid Oxidation of 5,14-Octadecanedione

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To study the effect of the nitric acid oxidation of a long paraffin chain containing two distantly placed carbonyl groups, 5,14-octadecanedione was oxidized with 50% nitric acid at 55°. The diketone was prepared in 50% yield by a modification of Cason's[1] method for preparing keto esters, whereby sebacyl chloride was added to di-*n*-butyl cadmium. Random attack on either side of the carbonyl groups of the diketone should have given 25% sebacic, 50% azelaic, and 25% suberic acid, and the theoretical amounts of the eight and ten carbon dibasic acids were found (Table I). However, far less than the theoretical yield of azelaic acid resulted, and smaller quantities of the four to seven carbon acids were also found.

TABLE I

Molar Yield of Dibasic Acids

Acid	Yield: %
Sebacic	25.8
Azelaic	14.6
Suberic	24.2
Pimelic	8.7
Adipic	7.0
Glutaric	8.2
Succinic	5.3
	93.8

Apparently azelaic acid was degraded to the smaller acids. This tendency of higher molecular weight dicarboxylic acids having an odd number of carbon atoms to break down more readily into shorter chain dicarboxylic acids than those having an even number of carbon atoms has been noted by others.[2]

EXPERIMENTAL

Preparation of Diketone. To 24.3 g. (1.0 mole) of magnesium covered with 150 ml. of dry ether was added 137 g. (1.0 mole) of *n*-butyl bromide in 350 ml. of ether over a period of 1.5 hr. The reaction mixture was refluxed for 15 min. and cooled, and to it was added 100 g. (0.54 moles) of anhydrous cadmium chloride. After the mixture was refluxed with stirring for 1 hr., the ether was stripped, 350 ml. of benzene was added, and, after the removal of 100 ml. of benzene by distillation, an additional 350 ml. of benzene was added. The mixture was stirred and refluxed for a few minutes to disperse solids, the heat was removed, the mixture was cooled with an ice bath, and 100 g. (0.40 moles) of sebacyl chloride, dissolved in 150 ml. of benzene, was added to the vigorously stirred solution over a 0.5 hr. period. The heat of reaction caused the mixture to reflux, although the flask was immersed in an ice bath. After the addition was complete, stirring and refluxing were continued for 2 hr., during which time it was necessary to apply heat.

To the product was added 600 ml. of ice water and then a large excess of 20% sulfuric acid. After the further addition of benzene and the separation into two phases, the undissolved solids were removed from each layer by filtration. The benzene solution was extracted successively with 200 ml. of water, 200 ml. of 5% sodium carbonate, 200 ml. of water, and 100 ml. of saturated sodium chloride solution and then passed through a column of anhydrous sodium sulfate. The aqueous phase was extracted with three 150 ml. portions of benzene, which were added to 200 ml. of a hot benzene solution of the gum in the original flask. This was washed and dried as above and added to the initial solution. After stripping the benzene the diketone was obtained by distillation as 56 g. (0.20 moles; 50%) of a colorless, hard, waxy solid boiling at 191° at 6.7 mm., and melting, after two recrystallizations from hexane, at 75.6–76.0°.

Anal. calcd. for $C_{18}H_{34}O_2$: C, 76.50; H, 12.08; mol. wt., 282. Found: C, 75.87; H, 11.87; mol. wt., 270.

Oxidation of Diketone. To 100 ml. of 50% nitric acid and 0.1 g. vanadium pentoxide in a 500 ml. 3-neck flask equipped with stirrer and vented reflux condenser was added 5.64 g. (0.05 moles) of 5,14-octadecanedione in small increments over a 4 hr. period while the temperature was maintained at 54.8–55.3°. The oxidation was marked by the evolution of brown nitrogen oxide fumes. Heating was maintained for another 2.5 hr.

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