one of the two possible causes. One of these can be the operation of the inductive effect of the two $PO(OR)_2$ groups attached to the methylene group. The other cause can be the partial double bond character of the P(O) linkage, which would permit the formation of an enolic structure involving the methylene group as well as the P(O) group, in a manner analogous to that customarily formulated for the sodio malonates and to which is usually attributed the stability and the ease of formation of such enolates. The very readiness of the reaction of the ester with potassium seems to argue for the latter explanation. Obviously if one assumes the completely semi-polar character of the P(O) linkages the formulation of the enol becomes impossible. Naturally, our observation is not the terminal solution of the true nature of the P(O) link, which has eluded such a solution after numerous experimental approaches.

The methylene activity in the diphosphonates has been made a starting point for further studies of alkylation of ordinary esters of aliphatic phosphonic acids, which coupled with a study of dipole moments of the compounds involved, may be expected to throw more light on the problem. The results of this work will be reported at a later date.

Experimental Part

Tetraethyl Methanediphosphonate.—This ester has been prepared earlier by Ford-Moore and Williams[4a] and by Schwarzenbach and Zurc.[4b] The method used by the former group was the most convenient for our purpose and the following description gives the details which were omitted by the previous workers in their synthesis in publication. Freshly distilled methylene iodide (103 g., b.p. 85–86° at 35 mm.) was rapidly added to 200 g. of triethyl phosphite (kindly supplied by the Virginia–Carolina Chemical Company; the product was redistilled before use) in a 500-ml. round-bottom flask, which was attached to a 16-inch Vigreux column. The mixture was heated rapidly to 160° by means of a pre-heated oil-bath. The colorless mixture acquired a dark brown-violet color which persisted for some 10 minutes, after which a vigorous reaction set in, with rapid evolution of ethyl iodide, which was collected in a cooled receiver. The reaction and the distillation were complete within 20 minutes, when the bath was heated to 170° for 10 minutes without causing any further change. Approximately 88 g. of ethyl iodide was collected for a 72.5% yield.

The reaction mixture was distilled under reduced pressure through a short fractionating column and gave, after redistillation, three fractions, as follows. The first fraction of 89 g. was composed in main of diethyl ethanephosphonate, b.p. up to 100° (mostly 98–100°) at 30 mm. The second fraction, which boiled at 95–135° at 0.5–0.4 mm. weighed 91 g. and was composed mainly (63 g.) of diethyl iodomethanephosphonate, b.p. 100° at 0.5 mm., 59% yield. The third fraction consisting of tetraethyl methanediphosphonate boiled at 135–137° at 0.4 mm. and weighed 20 g., for an 18% yield.

A somewhat smaller excess of triethyl phosphite (88 g. treated with 54 g. of methylene iodide) gave 31 g. of diethyl iodomethanephosphonate and 10 g. of tetraethyl methanediphosphonate. The large excess of the phosphite is quite essential for securing an appreciable yield of the disubstituted derivative.

Attempts to improve the yield of the latter by heating the isolated iodomethane derivative with triethyl phosphite were of dubious value, for the products were composed largely of diethyl ethanephosphonate and the iodomethane derivative, with only very small amounts of the diphosphonate. This result is in accord with the known sluggishness of the halogen in halomethanephosphonates. It also indicates that the Arbuzov–Michaelis reaction with dihal-

ides essentially completes itself in the initial stage, at least with methylene iodide, and is not a true two-step reaction.

Alkylation of the Diphosphonate.—The diphosphonate (20 g.) was diluted with one volume of dry xylene and the solution was added over a 15-minute period to 2.7 g. of sliced potassium suspended in 250 ml. of dry xylene. The reaction evolved an appreciable amount of heat and resulted in an initial formation of a light flocculent precipitate which was largely dissipated after two hours required for completion of the reaction. The mixture was gently heated for the last few minutes to facilitate the reaction. (If the mixture is heated and the metal is kept in molten state, the addition of the diphosphonate causes a very vigorous reaction and the evolved gas causes severe foaming.)

The mixture was then treated with 20 g. (excess) of n-butyl bromide and was stirred for three hours without any visible change. The flask was then heated cautiously to the reflux temperature and the heating was continued for 3.5 hr. at which time a definite precipitate of potassium bromide formed. This was filtered off and the filtrate was fractionated, yielding 14 g. of unreacted ester and 5 g. of diethyl pentane-1,1-diphosphonate, a colorless viscous liquid, b.p. 147–149° at 0.3 mm., n^{20}D 1.4428. This was hydrolyzed by refluxing overnight with 50 ml. of concentrated hydrochloric acid and evaporation to dryness with an infrared lamp. The product was recrystallized twice from water by repeated evaporation to remove any residual hydrochloric acid. The extremely hygroscopic pentane-1,1-diphosphonic acid was obtained in the form of waxy colorless needles which, after drying in high vacuum at 100°, soften at 143° and melt at 163–165°. The product gave a sharp depression of mixed melting point with methanediphosphonic acid.

Analytical.—The acid was titrated electrometrically to pH 5 according to Schwarzenbach.[4b] Calcd. for BuCH(PO_3H_2)$_2$: P, 26.7; equiv. wt., 116. Found: P, 26.5, 26.5; equiv. wt., 114, 114.5.

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The Growth and Analysis of Barium Oxide Crystals Containing a Stoichiometric Excess of Barium[1]

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In studying the possible existence of a suboxide of barium, Schriel[2] obtained small crystallites of barium oxide by dissolving BaO in molten barium metal. These crystallites were colored deep red, and contained a stoichiometric excess of barium in the crystal lattice. Schriel's analysis of these crystals showed that they contained from 0.6 to 1.3% excess barium. As a result of the present work, these values were shown to be too high due to the presence of microscopic globules of free barium metal which were found embedded in these crystals. Because of the interest in barium oxide as a semiconductor, large crystals of this red barium oxide were desired, as well as an accurate method of determining the excess barium in the crystal lattice. By the method described below, crystals as large as 2 mm. thick by 1 cm.[2] have been grown at this Laboratory.

Experimental

Growth of Barium Oxide Crystals.—A mixture of 60% barium metal chips and 40% barium oxide was put into a steel crucible, 1.25 in. in diameter and 4 in. long, so that only half the crucible was filled. The crucible was covered, and the lower half placed into a molybdenum wire wound furnace. The entire system was evacuated to a pressure of less than 10^{-4} mm. and heated at about 900° for 60–80

(4) (a) A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947); (b) G. Schwarzenbach and J. Zurc, *Monatsh.*, **81**, 202 (1950).

(1) This work has been supported by the Office of Naval Research.
(2) M. Schriel, *Z. anorg. Chem.*, **231**, 313 (1937).

hours. The barium oxide first dissolved in the molten barium, and then as the barium evaporated and condensed at the top of the crucible, which was at a much lower temperature, a thick layer of red barium oxide formed at the surface of the solution. This layer consisted of a few large single crystals, and its thickness depended upon the amount of barium evaporated. The crystals were removed from the barium melt by dissolving the barium in a 2:1 toluene-absolute alcohol mixture. The function of the toluene was to retard the precipitation of barium ethylate. There was also a slight reaction between the barium oxide and the absolute alcohol[3]

$$BaO + 2C_2H_5OH \rightleftharpoons Ba(C_2H_5O)_2 + H_2O$$
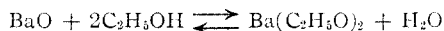
The water produced in this reaction causes a thin layer of barium hydroxide to be formed on the surface of the BaO crystals. However, this layer of hydroxide is easily removed by polishing the crystals.

Analysis of the Crystals.—In order to eliminate the error due to the occluded globules of barium metal mentioned above, the crystals were ground to a fine powder and washed with dry liquid ammonia, which dissolved the free barium metal without reacting with the barium oxide. The method used for the analysis was a modification of Berdennikowa's[4] method for oxide coated cathodes. The barium was placed into the sample tube of the apparatus shown in Fig. (1). After evacuating and outgassing the system, which has a total volume of 35 cc., the water in the liquid nitrogen trap was distilled into the sample tube. As the barium oxide dissolved, the excess barium reacted with the water to form hydrogen gas

$$Ba + 2H_2O \longrightarrow Ba(OH)_2 + H_2$$
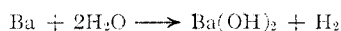
After the barium oxide was completely dissolved, the water was recondensed in the liquid nitrogen trap, and the pressure of the hydrogen gas was measured with a thermocouple vacuum gage. The percentage of excess barium was calculated from the amount of hydrogen gas present. All the work on barium oxide was carried out either in a dry-box or in a water-free atmosphere.
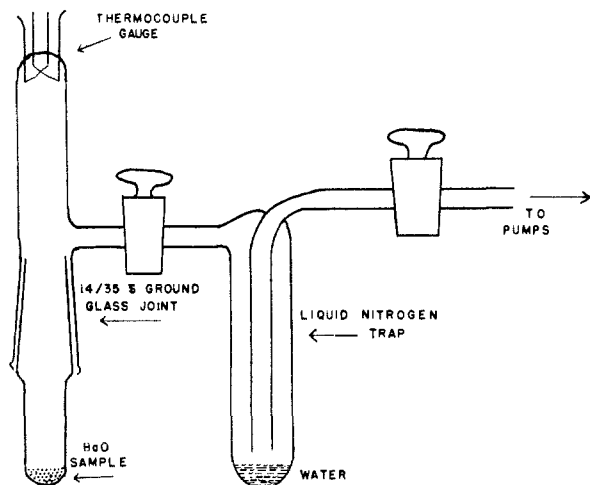

Fig. 1.

Discussion

Because the crystals were not perfectly homogeneous, the amount of barium in stoichiometric excess varied slightly from crystal to crystal within the same crystal growing run. Table I gives the percentages by weight of excess barium for two crystal growing runs. The three values given for run 48 represent three separate crystals taken from different sections of the surface layer of barium oxide.

Optical absorption measurements taken on these

(3) G. F. Smith, *Ind. Eng. Chem., Anal. Ed.*, **1**, 72 (1929).
(4) T. P. Berdennikowa, *Physik. Z. Sowjetunion*, **2**, 77 (1932).

TABLE I

Run no.	Time, hr.	Temp., °C.	Excess barium, %
35	60	890–910	0.14
48	73	880–905	.091
			.085
			.104

crystals by Kane[5] indicate that the excess barium is not present as colloidal aggregates, as believed by Schriel, but either as interstitial barium atoms or as oxygen vacancies in the lattice. More recent investigations (to be published soon) at this Laboratory, however, indicate that the interpretation of Kane's experiment may be more complicated.

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A Study of the Periodate Method for Determining End-group Values[1]

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The use of periodate for the determination of the degree of branching of certain carbohydrate substances such as starch and glycogen is based on its reaction with those monosaccharide units which contain alcohol groups on three adjacent carbon atoms and the resultant formation of a molecule of formic acid. Since in these polymers only the terminal glucose units have this necessary configuration, the amount of formic acid produced becomes a measure of the average length of the glucose chains, or of the degree of branching of these substances.

Many modifications of the periodate method have been proposed. These differ in the conditions of the oxidation reaction and in the method used for the determination of the formic acid. Formic acid has been determined after separation by steam distillation from the reaction mixture[2] and also iodometrically[3,4] but it is usually titrated directly with alkali after excess periodate is removed by reaction with ethylene glycol. The procedures employing direct titration variously specify that for quantitative recovery of formic acid, titration must be performed with different indicators to end-points of about pH 5.5,[4,5] pH 6.0,[6] pH 8.0,[7] and pH 8.2.[8] However, the titration curve of pure formic acid shows that it is quantitatively titrated at any of these pH values and that the choice of end-point should have little, if any, influence on the quantitative titration. The different modifications appear to give widely different end-group values. In this

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(7) K. H. Meyer and P. Rathgeb, *Helv. Chim. Acta*, **31**, 1540 (1948).
(8) A. Jeanes and C. A. Wilham, THIS JOURNAL, **72**, 2655 (1950).