that colloidal ceric polymers slowly form in perchloric acid media.[13] It is not surprising that these polymers cannot be detected by light scattering, because the particles formed would have to be quite small and at a very low concentration. It is most likely that the oscillations can be explained by formation and dissolution of colloidal particles or by some reaction that is dependent on their surface areas.

Experimental Section

Materials.—Bromomalonic and dibromomalonic acids were prepared according to the directions of Conrad and Reinback.[14] The aqueous solution of cerous bromate was prepared by mixing a solution of cerous sulfate with barium bromate and filtering off the barium sulfate. All other materials were of the highest purity available from commercial sources.

Methods.—All kinetic studies were performed in 3 N sulfuric acid at 30° in either a Gilford 2000 or Cary 15 spectrophotometer. The reactions were followed by observing the appearance or disappearance of the absorbance at 320 nm due to ceric ion as a function of time. The molar absorptivity at this wavelength is 5520.[15] The initial cerous ion concentration was measured spectrophotometrically at 253.6 nm where its molar absorptivity is reported[16] to be 685.

The light-scattering experiments were carried out in a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer, and the computer simulations were performed on an Electronic Associates, Inc. TR-20 analog computer.

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Notes

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The Photolysis of Two Diphosphonates

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Two reports of the photolytic reaction of monophosphonates have appeared in the literature. One report describes the liberation of orthophosphate from 2-aminoethanephosphonic acid.[1] A low concentration of hydrogen peroxide was added to provide excess oxygen during irradiation with a high-pressure mercury lamp. The photolysis described in ref 1 was used after a conventional inorganic phosphate analysis to convert organically combined phosphorus to phosphate, thus allowing the measurement of as little as 0.5 ppb of organic phosphorus in ocean water. No identification of the organic residue from 2-aminoethylphosphonic acid photolysis was made. Linear inorganic polyphosphates with between 3 and 70 phosphorus atoms in the chain were shown to be inert to chain depolymerization as a result of irradiation. Sunlight or ultraviolet irradiation converts methylphosphonic acid and other phosphonate derivatives into a form presumed to be orthophosphate.[2] The ozonolysis of methylphosphonic acid is reported to produce orthophosphoric acid, carbon dioxide, and water.[3] This reaction was very slow and converted less than 2% of the phosphonate to phosphate.

The photolytic reactions of alkyl phosphates have been studied more extensively. The photolysis of ethyl dihydrogen phosphate in water produced acetaldehyde, hydrogen, and phosphoric acid.[4] The primary photochemical process was the ejection of a hydrogen atom from the CH_2 group of an excited ethyl phosphate molecule. The yield of phosphoric acid was 100% throughout the pH range. The acetaldehyde produced by photolysis decomposes photolytically to methane and carbon monoxide, but this reaction has only a minor effect on the yield of acetaldehyde. The presence of excess oxygen in the ethyl phosphate solution during photolysis did not significantly change the reaction products.

The effect of photochemically generated hydroxyl radicals from hydrogen peroxide on deoxyribonucleic acid and simple model substances, including ethyl phosphate esters, has been reported.[5] Oxygen has a marked effect if the irradiation is performed in quartz tubes. Formaldehyde, acetaldehyde, and acids, in lesser quantities, were produced with phosphate from the irradiation of diethyl phosphate. The mechanism proposed describes the initial reaction as the abstraction of a hydrogen atom from the alkyl chain by the hydroxyl radical. Although the liberation of inorganic phosphate is indirect and results from an oxidation of the alkyl group of ethyl dihydrogen phosphate, there was no lag between the irradiation and the liberation of phosphate. In cases where one ester–phosphate bond has to be broken, the relation between phosphate liberated and time of irradiation was linear from the start. This indicated that the oxidation products of the initial stages of the process were so unstable that fission of the P–O–C bond followed almost immediately. It was also noted that

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photoradicals depolymerize sodium polyphosphate; therefore, direct radical attack on the P–O–P bond is possible in addition to the action on P–O–C bonds, although the former is probably not very important. Though this depolymerization contradicts the irradiation effect on linear polyphosphates in ref 1, no attempt was made here to resolve this aspect.

Present Work

This brief study of the photolysis of two diphosphonates, ethane-1-hydroxy-1,1-diphosphonate (EHDP) and methylenediphosphonate (MDP), is a part of a more extensive study of phosphonate reactions of analytical utility. The effects of hydrogen peroxide and oxygen on the reaction are reported. The phosphorus-containing reaction product is identified and is the same as that from the photolysis of monophosphonates and phosphate esters. Some properties of the other reaction products are discussed. A reaction path, which does not require hydrogen atom abstraction as proposed for ethyl dihydrogen phosphate, is discussed.

Experimental Section

EHDP and MDP were prepared by the syntheses described in ref 6 and 7, respectively. Tetramethyl methylenediphosphonate was prepared by an orthoformate reaction[8] and dimethyldodecylphosphine oxide was prepared by the trialkyl phosphite–methyl Grignard synthesis.[9] Their purity was established by elemental analyses, ^{31}P nmr, and thin layer chromatography. Photolysis experiments in distilled, deionized water were conducted at two levels of diphosphonate concentration. EHDP and MDP were at about 4000 ppm for the reactions in Figure 1. EHDP at 5% by weight in D_2O was used when the reaction was studied by ^1H and ^{31}P nmr techniques. The proton spectra was taken using a tetramethylsilane (TMS) capillary reference signal.

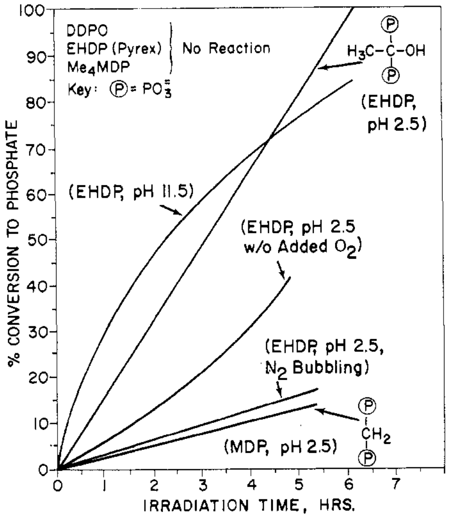

Figure 1.—Photolysis rates of EHDP and MDP. All reactions were oxygenated unless otherwise indicated. The actual protonated forms of EHDP at pH 2.5 and 11.5 can be determined from the acid dissociation constants ($pK_{a_1} = 1.0$, $pK_{a_2} = 3.06$, $pK_{a_3} = 7.34$, and $pK_{a_4} = 11.53$).

In most experiments, an oxygen bubbler was placed directly into the solution during irradiation in a 25-ml quartz flask with either a 200-W (Hanovia 654A) or a 450-W (Hanovia 679A) high-pressure mercury lamp. The quartz flask was connected to a 300-mm Liebig condenser (water circulation) and positioned about 5 cm from the center of the mercury lamp. The entire assembly was surrounded by a glass cylinder whose inside surfaces were covered with aluminum foil. Aliquots of the reaction mixture were removed without interrupting the photolysis by withdrawing 2-ml samples from the open end of the condenser with a syringe and Teflon capillary tubing. In all irradiation experiments, sufficient heat was generated to reflux the solution.

The amount of phosphorus species produced during photolysis was quantitatively measured by chemical analyses. The amount of orthophosphate produced was measured by phosphomolybdate colorimetry. When present, excess hydrogen peroxide was destroyed before phosphate analyses by the addition of catalytic platinum. Under the conditions used, phosphomolybdate does not form with phosphonate phosphorus. The total phosphorus level (*viz.*, the sum of phosphate and phosphonate) was measured before and/or after photolysis by the Carius fusion technique. Thus, a typical 5-hr irradiation experiment yielded data for the amount of orthophosphate before irradiation, for the amount of orthophosphate on aliquots withdrawn hourly, and for the total phosphorus level (Carius) after the fifth hour. The ppm phosphorus produced was calculated from the orthophosphate concentration as the per cent total phosphorus (from Carius analysis) converted to phosphate. These data are shown in Figure 1 for EHDP and MDP.

The proton and phosphorus nmr spectra were obtained on aliquots withdrawn during the irradiation of a 5% EHDP solution in D_2O. The ultraviolet spectrum of EHDP and the infrared spectra of the reaction mixture or products were obtained using normal procedures.

Results

Several variations in the experimental conditions affect the rate of phosphate formation during irradiation of EHDP. When the EHDP was heated to reflux for 5 hr without mercury lamp irradiation, no phosphate was produced. Hydrogen peroxide does not convert EHDP to phosphate. Thus, the reaction is a photolytic process and is not a thermal process.

When Pyrex flasks were substituted for quartz flasks, only 1.5% of the EHDP reacted in 5 hr. Thus, the favorable photolytic wavelength is less than about 2800 Å. The most intense line in the 200-W mercury lamp between 2800 and 2224 Å is at 2537 Å, rated at 1.1 W.[10] There are 11 other mercury lines between 2800 and 2224 Å emitted by the 200-W lamp[10] each producing less than 0.75 W. An experiment using a low-pressure 2537-Å mercury lamp rated at about 0.9 W produced no rearrangement, indicating that the 2537-Å line is not the exciting line. The absorption spectrum of EHDP is weak in the ultraviolet region with a maximum at 2500 Å having a molar absorptivity of 0.625.

Two factors were found to increase the reaction rate: the addition of excess hydrogen peroxide and the addition of excess oxygen.

Effect of Hydrogen Peroxide.—The addition of hydrogen peroxide before photolysis increases the rate of orthophosphate production more than either the continuous addition of oxygen or increasing the pH. Rearrangement of 0.2% EHDP in 1% H_2O_2 at pH 6.13 was 80% complete in 30 min. Three hours of irradia-

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tion was required for 80% reaction of the same EHDP solution in the absence of hydrogen peroxide.

Effect of Excess Oxygen.—The rate of EHDP rearrangement in the presence of oxygen is about twice as fast as the rearrangement when no oxygen is added during irradiation and nearly 5 times as fast as when the oxygen concentration is decreased by nitrogen bubbling during irradiation. This is shown in Figure 1.

Product Study.—The phosphonate portion of EHDP is rearranged to orthophosphate, based on orthophosphate chemical analysis and ^{31}P nmr data. Based on chemical analyses, orthophosphate is also produced by MDP photolysis.

The infrared spectrum shows the presence of a carbonyl function and carbon–hydrogen bonds in the organic reaction product(s). The ^1H nmr spectra show a regular decrease in the triplet signal characteristic of EHDP (τ 7.9) and the appearance of a singlet resonance signal at τ 7.5. In the interval between 50 and 75 hr of irradiation, the EHDP signal disappears, leaving the τ 7.5 peak as the signal from the product. This τ 7.5 peak at 5% concentration in D_2O with a TMS capillary is identified as acetic acid.

Discussion

The rate of rearrangement for EHDP, which contains the hydroxyl group, is faster than that for MDP which does not have this structural feature. Though the presence of the hydroxyl group leads to a faster rearrangement rate, perhaps by stabilizing an intermediate, it cannot be the only structural feature that leads to rearrangement If the phosphonate is not ionic, as in the tetramethyl ester of MDP, or if the phosphorus bonded to carbon is not in a high oxidation state, as in dimethyldodecylphosphine oxide (DDPO), no reaction occurs.

The primary photochemical processes of hydrogen peroxide are described in ref 11. In aqueous solution and in the energy region produced by mercury lamps, hydrogen peroxide undergoes homolytic dissociation of the peroxide bond to produce two hydroxyl radicals. Thus, hydroxyl radicals from hydrogen peroxide are probable species during these photolysis experiments. Calvert and Pitts also reported that the photolysis of water in all wavelength regions leads to hydroxyl radicals and hydrogen atoms though the energy state of the hydroxyl radical and the quantum yield of this reaction depends on the wavelength of light used for irradiation.

These primary photochemical processes reported to occur in aqueous solution and in the presence of hydrogen peroxide indicate that hydroxyl radicals will be important consequences of this photolysis experiment and support our experimental observations that hydrogen peroxide promotes the reaction but is not required for rearrangement.

It is not possible to define a reaction mechanism on the basis of the data reported here. The accelerative effect of hydrogen peroxide and oxygen on the reaction rate suggests that hydrogen atom abstraction is not as important to the photolysis of diphosphonates as it is reported to be for ethyl dihydrogen phosphate. Acetic acid is tentatively identified as the predominant organic residue. No direct evidence of acetaldehyde or paraldehyde as precursors to acetic acid was found.

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Some Observations on Ligand-Exchange Reactions of Bis-1,2-Dithiolene Complexes

BY A. L. BALCH[1]

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Recent studies have shown that ligand-exchange reactions can be effected between bis-1,2-dithiolene complexes in poorly coordinating solvents.[2,3] At room temperature these exchange reactions are generally slow for planar complexes. The sluggishness of these reactions was first demonstrated for nickel complexes[3] and the data in Table I show that exchange is also slow in the case of planar complexes of copper, gold, palladium, and platinum.

Information on the dithiolene ligand-exchange for some five-coordinate adducts[4] of the type (base)-$CoS_4C_4R_4^-$ is also set out in the table. The presence of additional base serves to retard the rate of attainment of equilibrium, but, within experimental error, the excess base does not affect the position of equilibrium. Similar results were obtained for the analogous five-coordinate iron adducts, but quantitative, reliable data are not available because of the susceptibility of the apical bases to oxygenation.[5]

Exchange reactions involving the dimeric bis-dithiolene complexes of iron and cobalt, which have the structure shown in Figure 1,[6] occur in two steps which require, respectively, seconds and hours to reach equilibrium. Figure 2 shows the region of the $Co_2S_8C_8R_8^{2-} \rightleftarrows Co_2S_8C_8R_8^- + e^-$ wave for a solution pre-

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