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Observations on an Oscillating Reaction. The Reaction of Potassium Bromate, Ceric Sulfate, and a Dicarboxylic Acid

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The oscillating reaction involving potassium bromate, ceric sulfate, and malonic acid has been reinvestigated. Other dicarboxylic acids were found to give periodic behavior under similar conditions. The separate reactions that make up the oscillating system have been examined. The reaction of Ce(IV) with dicarboxylic acids follows Michaelis-Menten kinetics in accord with complex formation followed by an oxidation reaction. The reaction of Ce(III) with bromate exhibits a lag phase and product inhibition [by Ce(IV)]. The kinetics for this reaction are not quantitatively reproducible. The sensitivity of the oscillating system to agitation suggests that this heretofore considered homogeneous system involves a degree of heterogeneity. Previous rationales to explain the nature of the oscillation have been experimentally disproven and shown to be theoretically untenable by computer simulation.

Oscillating reactions have been of interest to biologists and chemists alike, as a plausible way of explaining biological clocks and the external rhythms associated with them. The first kinetic scheme that could explain oscillating reactions was proposed by Lotka[2] in 1920. This mechanism as shown in eq 1 was used to explain ecological oscillations. In eq 1 G represents

$$\begin{gathered}[\mathrm{G}] + \mathrm{A} \xrightarrow{k_1} 2\mathrm{A} \\ \mathrm{A} + \mathrm{B} \xrightarrow{k_2} 2\mathrm{B} \\ \mathrm{B} \xrightarrow{k_3}\end{gathered} \qquad (1)$$

grass kept in constant supply which is eaten by animal A which reproduces. Animal B eats animal A to reproduce and eventually dies. Although this kinetic scheme dominated theoretical studies for nearly 50 years, no reactions were found which satisfy the conditions of eq 1.

The first oscillating reaction believed to occur in a homogeneous solution involved decomposition of H_2O_2 by I_2.[3] Subsequent investigation revealed the reaction to involve a heterogeneous system catalyzed by dust.[4] On reinvestigating this reaction Peard and Cullis[5] suggested that the oscillation was due to the physical removal of iodine by the evolving oxygen. More recently Degn[6] has shown stirring has no effect on this reaction indicating that it is homogeneous. He suggested the oscillation is caused by quadratic branching in a free-radical chain reaction.

Results of previous investigations[7,8] were interpreted to indicate that the oscillatory appearance of Ce(IV) in a solution of ceric sulfate, potassium bromate, and malonic acid in dilute sulfuric acid to be homogeneous. In this reaction ceric ion is reduced by reaction 2, and cerous ion is oxidized according to reaction 3. Reaction 2 is reported[9] to be first order when malonic acid is in excess. According to Zhabotinskii[7] reaction 3 exhibits an induction period and is autocatalytic. The bromine produced in reaction 3 rapidly brominates malonic acid. Degn[8] explained the oscillatory nature of this reaction as follows. The oscillation is caused by the inhibition of reaction 3 by dibromomalonic acid formed by the reaction of bromine produced in reaction 3 with malonic acid. Once reaction 3 is stopped or nearly stopped, the production of bromine and thus dibromomalonic acid ceases. After a while the dibromomalonic acid decarboxylates producing dibromoacetic acid which does not inhibit reaction 3 as much as dibromomalonic acid and reaction 3 starts again. Thus, the increase in the concentration of ceric ion is caused by reaction 3 when it is not inhibited and the decrease in ceric ion is caused by reaction 2 when reaction 3 is inhibited.

$$\mathrm{CH_2(COOH)_2 + 6Ce(IV) + 2H_2O \longrightarrow 2CO_2 + HCOOH + 6Ce(III) + 6H^+} \qquad (2)$$

$$\mathrm{10Ce(III) + 2BrO_3^- + 12H^+ \longrightarrow 10Ce(IV) + Br_2 + 6H_2O} \qquad (3)$$

Since this reaction provides a plausible model for circadian rhythms and since, *a priori*, the suggestions of Degn[8] appeared unlikely, the phenomena were reinvestigated.

Results

Complete System.—The reactions of malonic, citric, or maleic acids with ceric sulfate and potassium bromate in 3 *N* sulfuric acid are reported[7] to be periodic. We have confirmed these results and also found that malic, bromomalonic, and dibromomalonic acids will react with these reagents in a periodic manner. The conditions employed with malonic, citric, and maleic acids to provide an oscillatory appearance of Ce(IV) failed to do so with oxalic, tartronic, 3-hydroxypropionic, succinic, and pyruvic acids.

The oscillating reaction involving malonic acid was investigated in greater detail. Although the concentrations of the reactants necessary to obtain oscillation

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[1] Postdoctoral Fellow of the National Institutes of Health, 1969–1970.

[2] A. J. Lotka, *J. Amer. Chem. Soc.*, **42**, 1595 (1920).

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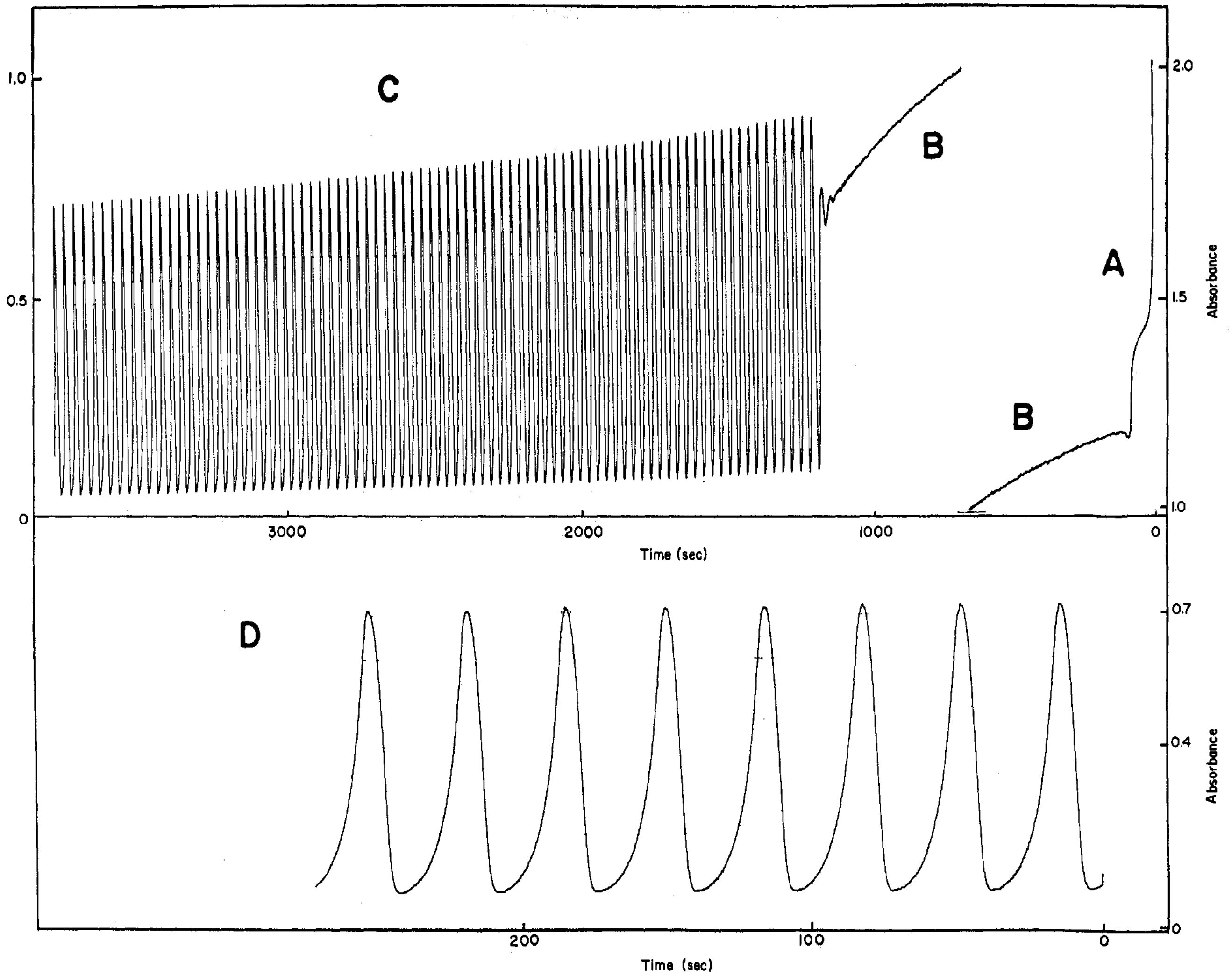


Figure 1.—A trace of absorbance *vs.* time for the oscillating reaction of 0.00011 *M* ceric sulfate, 0.1 *M* malonic acid, and 0.03 *M* potassium bromate in 3 *N* sulfuric acid at 30°: (A) the initial disappearance of ceric ion from 2 to 1 absorbance unit; (B) the induction period; (C) the oscillatory portion which continues for well over 500 oscillations; (D) an expanded portion of the oscillatory reaction showing the shape more clearly.

were not critical, the following concentrations were utilized in our experiments: 0.00015 *M* ceric sulfate, 0.03 *M* potassium bromate, 0.1 *M* malonic acid, dissolved in 3 *N* sulfuric acid. A typical plot of absorbance *vs.* time is found in Figure 1. The same general type of curve was reported by Degn.[8] The shape of the oscillations of this reaction is very sensitive to stirring. With continuous stirring the oscillations are very regular with the amplitude decreasing slightly with time. If the stirring is stopped the oscillations become irregular, and their amplitude decreases. If the reaction is stirred again the amplitude returns to normal as does the shape of the peak. This phenomenon is not caused by oxygen (bubbling oxygen, nitrogen, or carbon dioxide through the reaction mixture either prior to or after adding ceric sulfate had little or no effect on the shape of the absorbance *vs.* time curve).

Adding ground glass or dust to the mixture had no effect. Adding a drop of concentrated sodium carbonate to 3 ml of the mixture caused the solution to be supersaturated with CO_2. When the ceric sulfate is added to this mixture, there is a slight oscillation during the induction period, but this stops before the regular oscillations start. When a sufficient concentration (0.065 *M*) of tribromoacetic acid was added to the reaction mixture, oscillation occurred but the induction period disappeared. Adding bromine to the reaction mixture caused a shortening of the induction period, presumably due to the formation of the brominated malonic and acetic acids.

Once the oscillating reaction is started, addition of formic acid (to 0.04 *M*), trichloroacetic acid (to 0.02 *M*), or dibromomalonic acid (to 0.006 *M*) has no effect on the oscillations. However, adding dibromoacetic acid (to 0.04 *M*) decreases the amplitude of the oscillations by about 10%, but the period remains the same. The addition of bromine (0.001 *M*) causes a delay in the formation of ceric ion, but after this the normal period resumes. Attempts to detect particles by light scattering failed due to the excess scattering from the CO_2 bubbles formed in the reaction.

Reaction of Ceric Ion with Organic Acids.—The reaction of ceric sulfate with malonic acid[9] and citric acid[10] has been previously reported. Reinvestigation establishes these reactions to follow Michaelis–Menten-like behavior, *i.e.*, a plot of $1/k_{\text{obsd}}$ *vs.* 1/[malonic acid] is linear. This type of behavior is in accord with the mechanism of eq 4 where A represents the organic acid and $\text{Ce}^{\text{IV}}\text{A}$ represents a complex formed between ceric ion and the organic acid. Equation 5 is derived

$$\text{Ce(IV)} + \text{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ce}^{\text{IV}}\text{A} \xrightarrow{k_2} \text{Ce(III)} + \text{P} \qquad (4)$$

from eq 4 in the usual Michaelis–Menten manner, where

$$V = \frac{k_2[\text{A}][\text{Ce(IV)}_\text{T}]}{K_\text{m} + [\text{A}]} \qquad (5)$$

K_m is $(k_{-1} + k_2)/k_1$ and $[\text{Ce(IV)}_\text{T}]$ is the sum of [Ce(IV)] and $[\text{Ce}^{\text{IV}}\text{A}]$. Table I shows the values of K_m and $k_{\text{obsd max}}$.

TABLE I

VALUES OF K_m AND $K_{\text{obsd max}}$ FOR VARIOUS ORGANIC ACIDS

Acid	K_m, M	$k_{\text{obsd max}}$, sec^{-1}
Malonic	0.53	0.53
Citric	0.67	0.16
Bromomalonic	0.20	0.067

Bubbling oxygen through the reaction mixture containing citric acid and ceric ion causes no change in rate, so presumably oxygen has no effect on this reaction. A fivefold excess of dibromoacetic over malonic acid also does not affect the rate; however, when the concentrations of tribromoacetic acid and malonic acid are both 0.05 M, the rate is 0.033 sec^{-1} compared to 0.047 sec^{-1} when no tribromoacetic acid is present. Thus tribromoacetic acid inhibits this reaction slightly.

Reaction of Cerous Sulfate with Potassium Bromate.—The reaction of cerous sulfate with potassium bromate is a very complex process, as can be seen from Figure 2. The reaction shows an initial induction period, followed by a burst of Ce(IV) formation which is followed in turn by a much slower production of Ce(IV) until all Ce(III) is consumed. This slowing of the production of ceric ion will be referred to as the cutoff. When the concentration of potassium bromate is 0.005 M [Ce(III) at 3×10^{-4} M], the induction period is 7 ± 2 sec; however when the potassium bromate concentration is reduced to 0.001 M the induction period varies between 70 and greater than 9000 sec. This induction period was totally irreproducible, and bubbling oxygen or nitrogen through the reaction mixture did not change the situation.

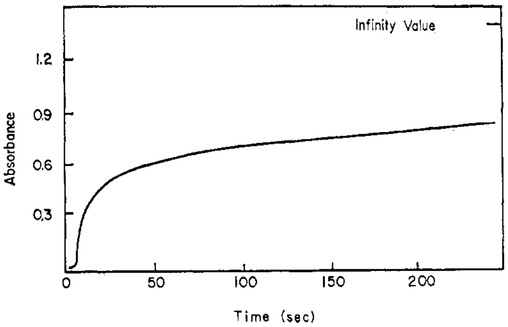


Figure 2.—Plot of absorbance at 320 nm *vs.* time for the reactions of cerous sulfate with 0.01 M potassium bromate at 30°.

The effect of organic acids on the induction period is quite strange. In the presence of 0.013 M malonic acid the induction period is increased from 7 to about 25 sec if cerous sulfate is the last component added. However, if the solution with the malonic acid in it is allowed to stand for 6 hr before the cerous sulfate is added, the induction period decreases to about 8 sec. This reaction mixture still oscillates indicating that the malonic acid was not consumed. If more malonic acid is added to this reaction mixture that has been allowed to stand, the induction period does not change; *i.e.*, it is still about 8 sec. In summary, 0.013 M malonic acid causes an increase in the induction period. If the reaction mixture containing the potassium bromate and malonic acid is allowed to age before the ceric sulfate is added, the induction period appears normal. Further addition of malonic acid did not increase the induction period. Similar results were found with formic, acetic, and trichloroacetic acids.

Even if the induction period is neglected, the reaction is still not simple, but at least it is reproducible. Since we have found no way of plotting the data to obtain an empirical rate law, our observations must be expressed qualitatively. (1) Decreasing the bromate ion concentration increased the induction period and also caused the cutoff to occur at a lower ceric ion concentration than usual. (2) Adding bromine in excess of that produced in the reaction caused an increase in the induction period but the cutoff was more gradual. (3) Running the reaction in 20% acetone–70% 3 N H_2SO_4 (v/v) made the cutoff almost disappear. (4) Adding ceric ions enhanced the cutoff (occurred in a shorter time period and at a higher cerous ion concentration). (5) When aqueous $\text{Ce(BrO}_3)_3$ was added instead of $\text{Ce}_2(\text{SO}_4)_3$, the results were the same. (6) The reaction was not affected by stirring. (7) Constant bubbling of oxygen, nitrogen, or carbon dioxide through the reaction mixture stopped the reaction after the burst. This was further investigated.

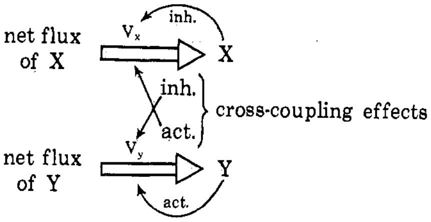
When nitrogen is bubbled through the reaction mixture of cerous sulfate and potassium bromate, a pseudo-second-order rate plot is obtained if the experimental infinity value is used. In the experiment described below, enough cerous ion to make the solution 5.85×10^{-5} M was added to a solution 0.01 M in potassium bromate. The infinity value of ceric ion was only 3.21×10^{-5} M; thus all the cerous ion was not converted to ceric ion. A plot of $(A - A_0)/(A_\infty - A)$ *vs.* time is linear if the induction period, about 9 sec is neglected. Thus the reaction appears to be second order in cerous ion.

Attempts to detect light scattering at 500 nm were inconclusive, even if the concentration of cerous sulfate added to 0.01 M potassium bromate was 1.5×10^{-3} M, which is 10 times greater than in the oscillating reaction.

(10) R. N. Mehrotra and S. Gosh, *Z. Phys. Chem.* (*Leipzig*), **224**, 57 (1963).

Discussion

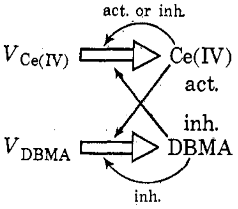
Higgins[11] has pointed out that oscillatory systems should be reducible to at least a two-variable problem which may be conveniently represented by net flux diagrams one of which is shown in (I), where X and Y are two species produced in a reaction and the principal arrows represent the net fluxes (reaction velocities V_x and V_y) for X and Y.



(I)

To determine if the concentration of X and Y will be periodic with time, one examines the "activational" (act.) and "inhibitional" (inh) interactions between X and V_x and Y and V_y and the activational and inhibiting cross-coupling effects operating between the processes constituting the fluxes V_x and V_y and species Y and X, respectively. Activational and inhibitional effects are defined[11] by positive or negative signs, respectively, of the following differential equations: $\partial V_x/\partial[X]$, $\partial V_y/\partial[Y]$, $\partial V_x/\partial[Y]$, and $\partial V_y/\partial[X]$. The first two derivatives represent the self-coupling terms, and the last two, cross-coupling terms. For a reaction to exhibit sustained oscillations the product of the cross-coupling terms must be negative, and the product of the self-coupling terms usually must be negative.[11] Let us now examine the mechanism proposed by Degn[8] for the periodic reaction between malonic acid, ceric ion, and bromate ion, in the light of these criteria.

The net flux diagram is shown in (II). The self-coupling term for the net flux of Ce(IV) will be inhibitory if reaction 2 is faster than reaction 3 and activational if (3) is faster than (2) because (3) is autocatalytic. The self-coupling term for dibromomalonic acid (DBMA) is inhibitory in the usual sense, *i.e.*, the more there is the faster it reacts. The cross-coupling terms are more complicated. For a fixed concentration of Ce(IV), DBMA inhibits the formation Ce(IV) *via* reaction 3. The effect of Ce(IV) on the net flux of DBMA is activational, because an increase in the concentration of Ce(IV) causes more Ce(III) to be produced by reaction 2, which increases the production of bromine by reaction 3 and thus the production of DBMA.



(II)

The important consideration is the product of the cross-coupling term $(\partial V_{DBMA}/\partial[Ce(IV)])(\partial V_{Ce(IV)}/\partial[DBMA])$. In this case the product is negative, and according to the theory of oscillating reactions[11] this mechanism proposed by Degn could show oscillatory behavior.

The proposed mechanism is however rendered unlikely by the observation that adding dibromomalonic acid to the reaction when it is oscillating has no effect on it, and both bromomalonic and dibromomalonic acids react with ceric sulfate and potassium bromate in a periodic manner.

In spite of this objection many attempts were made to simulate the oscillating reaction on an analog computer. Schemes of the type suggested by Degn,[8] in which reaction 3 is autocatalytic and inhibited by any or all of the various bromine derivatives of malonic acid, did not show oscillatory behavior.

Since adding ceric ion to the cerous sulfate–potassium bromate reaction increases the cutoff, it is likely that ceric ion is responsible for the cutoff. If this cutoff is incorporated in the previous scheme or used by itself to inhibit reaction 3, still no oscillations are observed.

(According to Higgins[11] the product of the cross-coupling terms must be negative. This can only happen in this case if reaction 2 inhibits reaction 3 or *vice versa*.) We have established that the products of reaction 3 and the bromine derivatives of malonic acid have little if any effect on reaction 2, so it may be that one of the products of reaction 2 is inhibiting reaction 3. This cannot be determined presently because the kinetics of the cerous ion–potassium bromate reaction are not at all understood by us. A complete understanding of this reaction is prerequisite to an understanding of the correct kinetic scheme for the oscillating reaction. Since the cerous sulfate–potassium bromate reaction is very complex and the induction period is irreproducible at low $[BrO_3^-]$, this information cannot be obtained. However, a computer simulation in which reaction 3 is autocatalytic and some product of reaction 2 inhibits it shows damped oscillatory behavior.

The irreproducibility of the lag phase for the bromate reaction suggests heterogeneity in this and also the oscillating reaction. In addition the marked increase of the cutoff by bubbling O_2, N_2, or CO_2 or addition of Ce(IV) would be in accord with Ce(IV) containing aggregrates formed from Ce(IV) produced at a gas–liquid interface. Also, the fact that the oscillating reaction is sensitive to stirring or shaking (reactions 2 and 3 are not) is only in accord with a degree of heterogeneity. It should be noted, however, that no particles could be detected by light scattering. This is of no great significance since CO_2 liberated in the course of the reaction would obliterate any scattering from particles. Also dust or ground glass have no effect on the oscillating reaction.

It is difficult to say what this (these) heterogeneous phase(s) might be, but it has been suggested[12] that an appreciable fraction of ceric ion in sulfate media (pH >2.5) can exist as a colloidal hydroxide or basic sulfate which is not in rapid equilibrium with the solution and

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(11) J. J. Higgins, *Ind. Eng. Chem.*, **59**, 18 (1967).

(12) E. L. King and M. L. Pandow, *J. Amer. Chem. Soc.*, **75**, 3063 (1953).

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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(16) H. L. Greenhaus, *et al.*, *Anal. Chem.*, **29**, 1531 (1957).

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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