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# Kinetics and Mechanism of Oxidations by Peroxydiphosphate. 2. Oxidation of Bromide in Aqueous Perchloric Acid Solution

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Peroxydiphosphate oxidizes bromide in aqueous perchloric acid medium according to $2P(VI) + 2Br^- \rightarrow 2P(V) + Br_2$. The rate is independent of the concentration of bromide and the rate-determining step is the hydrolysis of peroxydiphosphate to peroxymonophosphate. In the acid concentration range $2.5 > [HClO_4] > 0.1$ M, the predominant species is $H_2P_2O_8^{2-}$, but the reactive species is $H_3P_2O_8^-$. The rate law is $-d[\text{perox}]_T/dt = k_2[H_3P_2O_8^-] = (k_2/K_2)[H^+][\text{perox}]_T$, where $K_2$ is the second dissociation constant of $H_4P_2O_8$ and its least value was estimated to be 40. $k_2/K_2$ was found to be $(3.1 \pm 0.3) \times 10^{-4}$ s$^{-1}$ at 25 °C and $\mu = 2.5$ M.

## Introduction

It is only recently that the interest in the redox reactions involving peroxydiphosphate has developed and most of the work has been done by Edwards and co-workers.[1] Oxidations of arsenic(III)[2] and antimony(III)[3] are essentially hydrolytic reactions of peroxydiphosphate in which the rate is independent of the concentration of the reducing substance. These reactions are conspicuous by the absence of any free-radical mechanism. On the other hand, oxidation of vanadyl[4] ion is accompanied by the formation of a free radical, probably the radical ion $PO_4^{2-}$, and is dependent on the concentration of the reducing substance too. Oxidations of low-spin iron(II) complexes[5,6] show that the rate-determining step is the dissociation of the complex and that the redox reaction involving peroxydiphosphate occurs in a fast step. Oxidation of bromide was studied in view of the interesting results with iodide ion.[7]

## Experimental Section

Potassium peroxydiphosphate was a gift sample from the FMC Corp. It contained potassium phosphate and potassium fluoride as the impurities. Since the impurities had little effect on the rate, it was used as such. Its solution was prepared by direct weighing and standardized cerimetrically[8] as well as iodometrically.[9] The solution did not deteriorate or hydrolyze on keeping. All other chemicals were BDH AnalaR or E, Merck quality. All solutions were prepared in twice-distilled water, the second distillation being from the permanganate.

Perchloric acid, 70% AnalaR (Riedel), was used to vary the hydrogen ion concentration. Ionic strength was adjusted with sodium perchlorate prepared by neutralizing perchloric acid with sodium hydrogen carbonate.

BDH AnalaR sodium bromide was used for bromide.

## Kinetics Procedure

The experiments were conducted in stoppered Erlenmeyer flasks immersed in a thermostated water bath at 35 ± 0.1 °C, unless mentioned otherwise. The reaction was initiated by adding a known volume of peroxydiphosphate to a temperature-equilibrated mixture containing sodium bromide, perchloric acid, and other reagents of desired concentrations. The reaction could not be initiated by adding bromide in the end, since peroxydiphosphate undergoes hydrolysis.

The kinetics were followed by determining peroxydiphosphate cerimetrically from time to time. Aliquot (5 or 10 ml) portions were added to a mixture of 10 ml of acetone and 10 ml of saturated solution of sodium bicarbonate. A known volume of ferrous ammonium sulfate solution with excess sulfuric acid sufficient to yield 1.0 M solution was then immediately added. The unreacted iron(II) was titrated against cerium(IV) using *n*-phenylanthranilic acid as indicator.

Acetone was added to remove bromine which reacts[10] with iron(II) and interferes with the titration. The pH of the system was raised by the bicarbonate to arrest the reaction between the peroxydiphosphate and bromide. Peroxydiphosphate as such does not oxidize acetone in competition with iron(II), but the estimation of peroxydiphosphate in this way was always 76–77% of the cerimetric or iodometric assay. This, however, does not affect the nature of the results nor the rate constants. Further probing into the cause of this decreased assay of peroxydiphosphate showed that (1) acetone does not react with peroxymonophosphate, (2) there is no change in the assay if peroxydiphosphate and acetone are allowed different contact times, and (3) there is no change in the assay with different excess iron(II) solutions.

The first-order rate constants were calculated either by a plot of log [peroxydiphosphate] vs. time (the rate is independent of bromide concentration) or from the initial rates. The results were reproducible to ±6%. From here on [perox] has been used for [peroxydiphosphate].

Since the rate was independent of bromide concentration, it was necessary to carry out a few hydrolytic experiments to prove that the mechanism of the redox reaction is essentially hydrolysis of peroxydiphosphate. Although hydrolysis has been studied[11–13] exhaustively, experiments under identical conditions were necessary so that a comparison with the results of the redox reaction could be made. Reactions were initiated by adding peroxydiphosphate to a mixture containing requisite quantities of perchloric acid and sodium perchlorate but no bromide. The kinetics were followed iodometrically[14] in an acetate buffer of pH 4–5 in the presence of trace ammonium molybdate. Aliquot portions were added to requisite quantities of acetate, acetic acid, or sodium hydroxide (to neutralize excess perchloric acid in the reaction mixture) yielding the buffer. KI was added and the liberated iodine was titrated against thiosulfate. Since peroxydiphosphate slowly hydrolyzes even in a medium of pH 4–5, the first disappearance of blue color was noted.

Peroxydiphosphate hydrolyzes[15,16] to peroxymonophosphoric acid and then to hydrogen peroxide. In a medium of pH 4–5 peroxydiphosphate does not liberate iodine from iodide, peroxymonophosphoric acid does readily, and hydrogen peroxide does so slowly. Trace ammonium molybdate strongly catalyzes the reaction between hydrogen peroxide and iodide, and hence peroxymonophosphoric acid together with hydrogen peroxide could be estimated.

## Results

**Stoichiometry.** In 15 experiments different concentrations of peroxydiphosphate, bromide, and perchloric acid were mixed and kept for sufficient time for the completion of the reaction. The liberated bromine was swept by a current of nitrogen and led to a solution of KI. The iodine so liberated was titrated against thiosulfate. Excess of peroxydiphosphate in the reaction mixture was determined cerimetrically[8] and excess of bromide was determined[17] by titrating against a silver nitrate solution with eosin as indicator in a medium of pH 2.5–2.8. One mole of peroxydiphosphate required 1.98 ± 0.06 mol of bromide conforming to the equation $P_2O_8^{4-} + 2Br^- \rightarrow 2PO_4^{3-} + Br_2$.

**Table I.** Values of $10^4 k_0$ ($s^{-1}$) for Peroxydiphosphate-Bromide Reaction at Different [$H^+$]'s and Temperatures[a]

| | Temp, °C | | | |
|---|---|---|---|---|
| [$HClO_4$], M | 25 | 35 | 45 | 50 |
| 0.10 | 0.25 | 0.61 | 1.3 | 2.3 |
| 0.20 | | | 2.3 | |
| 0.25 | | 1.6 | | |
| 0.30 | | | 4.6 | |
| 0.40 | | | 7.2 | |
| 0.50 | 1.2 | 3.1 | 8.8 | 12.7 |
| 0.75 | | 5.7 | 11.5 | |
| 1.00 | 3.1 | 7.6 | 23 | 29 |
| 1.25 | | 10.5 | | |
| 1.50 | 4.6 | 12.5 | 32 | 41 |
| 2.00 | 6.2 | 16.5 | | |
| 2.25 | | 18 | 46 | |
| 2.50 | 8.9 | 21 | | 63 |

[a] [perox] = $4.38 \times 10^{-3}$ M; [$Br^-$] = 0.2 M; $\mu = 2.5$ M.

**Table II.** Values of $10^4 k_H$ ($s^{-1}$) for the Hydrolysis of Peroxydiphosphate at Different [$H^+$]'s and Temperatures[a]

| | Temp, °C | | |
|---|---|---|---|
| [$HClO_4$], M | 35 | 45 | 55 |
| 0.10 | 0.23 | 0.66 | 2.9 |
| 0.20 | 0.52 | 2.5 | 4.2 |
| 0.30 | 1.05 | 4.2 | 12.5 |
| 0.40 | 2.3 | 5.0 | 19 |
| 0.50 | 3.45 | 8.4 | 39 |
| 0.80 | 6.1 | 14 | 43 |
| 1.00 | 8.6 | 18 | 53 |
| 1.20 | 9.8 | 20 | 54 |
| 1.50 | 12.5 | 33 | 76 |
| 1.80 | 15 | 38 | 78 |
| 2.00 | 17 | 44 | 96 |
| 2.20 | 18 | 46 | 103 |
| 2.50 | 20 | 53 | |

[a] [perox] = $4.38 \times 10^{-3}$ M; $\mu = 2.5$ M.

**Peroxydiphosphate Dependence.** The concentration of peroxydiphosphate was varied from $8.7 \times 10^{-4}$ to $2 \times 10^{-2}$ M at three fixed concentrations (0.2, 0.1, and 0.05 M) of bromide, at constant [$HClO_4$] = 0.5 M, and at $\mu = 0.75$ M. A log–log plot of initial rate and [perox] showed an order of one with respect to peroxydiphosphate. A plot of log [perox] vs. time also yielded a straight line. The average first-order rate constant at [$HClO_4$] = 0.5 M, $\mu = 0.75$ M, and 35 °C was found to be $(3.1 \pm 0.1) \times 10^{-4}$ $s^{-1}$.

**Bromide Dependence.** The concentration of bromide was varied from $1.0 \times 10^{-3}$ to $2.0 \times 10^{-1}$ M at fixed [perox] = $4.38 \times 10^{-3}$ M, [$HClO_4$] = 0.5 M, and $\mu = 0.75$. The rate was found to be independent of the concentration of bromide.

**Hydrogen Ion Dependence.** Hydrogen ion concentration was varied with perchloric acid in the range 0.1–2.5 M at constant $\mu = 2.5$ M adjusted with sodium perchlorate. The rate increased with the increase of $HClO_4$. The results at four temperatures are given in Table I.

**Activation Energy and Entropy.** The reaction was studied at four temperatures, and the first-order rate constants at 25, 35, 45, and 50 °C and at [$HClO_4$] = 0.5 M and $\mu = 0.75$ M were found to be $1.2 \times 10^{-4}$, $3.1 \times 10^{-4}$, $8.8 \times 10^{-4}$, and $1.3 \times 10^{-4}$ $s^{-1}$, respectively. The overall energy and entropy of activation were found to be $19.8 \pm 0.6$ kcal/mol and $7.9 \pm 2.4$ cal/(deg mol), respectively.

## Discussion

The results of hydrolytic study at different temperatures and hydrogen ion concentrations are given in Table II. A comparison with Table I would show that in general the redox reaction is nothing but a hydrolytic reaction. The nondependence of rate on bromide concentration further supports the above contention. If peroxydiphosphate is allowed to hydrolyze and then bromide is added, immediate reaction occurs. Battaglia[18] reported a value of 0.5 $s^{-1}$ for $k_{obsd}$ for the reaction $H_3PO_5$–$Br^-$ at about 0.3 M $H^+$, 25 °C, and $\mu = 1.5$ M. The corresponding value for the hydrolytic reaction at the same temperature and hydrogen ion concentration and at $\mu = 2.5$ M is not more than $1.2 \times 10^{-4}$ $s^{-1}$. Thus the reaction step in which the oxidation of bromide occurs is several times faster than the hydrolytic step. Another fact to be noted is that the overall energy of activation (19.8 kcal/mol) is similar to that reported (18.3–19.5 kcal/mol) for the hydrolytic reaction.

The peroxydiphosphate anion is tetrapositive and the third ($K_3$) and fourth ($K_4$) dissociation constants are reported[19] to be $6.6 \times 10^{-6}$ and $2.1 \times 10^{-8}$, respectively. It has not been possible to determine the values of the first ($K_1$) and second ($K_2$) dissociation constants but Crutchfield and Edwards[19] have estimated them by comparing the corresponding values of $H_4P_2O_6$ and $H_4P_2O_7$ and by extrapolation. The values are approximately 2 and 0.3, respectively, at 25 °C. However, later Venturini et al.[20] showed that the method of Crutchfield et al.[19] was in error and that $K_2$ should be at least 3. Generally three species $H_4P_2O_8$, $H_3P_2O_8^-$, and $H_2P_2O_8^{2-}$ are said to exist under the acid conditions employed and they are correlated by the equilibria

$$H_2P_2O_8^{2-} + H^+ \xrightleftharpoons{1/K_2} H_3P_2O_8^- \tag{1}$$

$$H_3P_2O_8^- + H^+ \xrightleftharpoons{1/K_1} H_4P_2O_8 \tag{2}$$

Hydrogen ion dependence will show which are the species mainly present and which are the species contributing to the rate of hydrolysis. The complete rate law considering all of the species to be reactive is

$$-[\text{perox}]/dt = \frac{[\text{perox}](k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2}{K_1K_2 + K_1[H^+] + [H^+]^2}$$

or

$$k_0 = \frac{k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2}{K_1K_2 + K_1[H^+] + [H^+]^2} \tag{3}$$

where $k_0$ is the pseudo-first-order rate constant. For the acid concentration range investigated, a plot of $k_0$ vs. [$H^+$] yields straight lines passing through the origin at all four temperatures. Thus the rate law (3) must reduce to either (4) or (5).

$$k_0 = \frac{k_2K_1[H^+]}{K_1K_2} = \frac{k_2}{K_2}[H^+] \tag{4}$$

$$k_0 = k_3K_1K_2[H^+]^2/K_1[H^+] = k_3K_2[H^+] \tag{5}$$

In the first case (eq 4) $H_2P_2O_8^{2-}$ is the species mainly present and $H_3P_2O_8^-$ is the species contributing to the rate. In the second case (eq 5) $H_3P_2O_8^-$ is the species mainly present and $H_4P_2O_8$ is the species which contributes to the rate. If 95% or more of any species is considered to be a predominant proportion, for the first case $K_2 > 40$ and $K_1/K_2 > 1$ and for the second case $K_2 < 0.005$ and $K_1 > 80$. A value of less than 0.005 for $K_2$ is improbable since Crutchfield and Edwards[19] found no inflection in the titration curves corresponding to $H_3P_2O_8^-$. Thus it appears that $K_2$ should be at least 40 and $K_1$ larger than 40, and the mechanism of eq 6–8 may be proposed for the reaction. The values of $k_2/K_2$ obtained from

$$H_2P_2O_8^{2-} + H^+ \xrightleftharpoons{1/K_2} H_3P_2O_8^- \tag{6}$$

$$H_3P_2O_8^- + H_2O \xrightarrow{K_2} H_2PO_5^- + H_3PO_4 \tag{7}$$

$$H_2PO_5^- + Br^- \xrightarrow{\text{fast}} \text{products} \tag{8}$$

the plots of $k_0$ vs. $[H^+]$ were found to be $(3.1 \pm 0.3) \times 10^{-4}$, $(8.0 \pm 0.6) \times 10^{-4}$, $(19 \pm 1.1) \times 10^{-4}$, and $(26 \pm 1) \times 10^{-4}$ $s^{-1}$ at 25, 35, 45, and 50°, respectively.

It appears that the nucleophilic attack of OH of the water on phosphorus of the peroxydiphosphate is much easier, as suggested by Franchuk and Brodskii,[11] than the nucleophilic attack[21] of bromide on the oxygen of the peroxydiphosphate; hence the reaction prefers the hydrolytic path rather than a direct redox reaction. The attack by OH on P would be facilitated by the less negative charge on the peroxydiphosphate ion resulting in catalysis by the hydrogen ion. The reaction, therefore, is faster with species $H_3P_2O_8^-$. The mechanism is similar to that of phosphate esters and related compounds.[22]

A comparison of the results of the present investigation with those of the oxidation of iodide[7] shows little similarity between the two. The latter involves a rate law of three terms, of which one refers to hydrolytic reaction and the other two refer to direct reactions of iodide with $H_3P_2O_8^-$ and $H_2P_2O_8^{2-}$. The difference in character probably lies in the difference of the polarizability of the iodide and bromide ions, and thus iodide serves as a better nucleophile[23] for attack on oxygen of the peroxydiphosphate.

Formation of phosphate ion radical $PO_4{\cdot}^{2-}$ has been reported in the oxidation of $Fe^{II}$ complexes[7,24,25] and in the photolytic oxidation[26] of water, but no such evidence was found in the present investigation or in the oxidations of arsenic(III)[2] and antimony(III)[3] (absence of any effect of acrylamide on the rate). There is no evidence also in the hydrolytic studies and hence this is another support for the mechanism of the redox reaction suggested earlier.

A comparison of peroxydisulfate and peroxydiphosphate reactions may be of some interest. The decomposition of peroxydiphosphate[27] is slower than that of peroxydisulfate[28] and both of them involve free-radical ions.[28,29] All redox reactions studied so far involving peroxydiphosphate are faster. Peroxydisulfate requires the use of silver(I) as catalyst for the oxidations of manganese(II)[30,31] and vanadyl ions,[32] whereas peroxydiphosphate does so readily even without catalyst. Peroxydiphosphate hydrolyzes more readily than peroxydisulfate.[34] Catalysis by silver(I) and probably by copper(II), also, appears to be a common feature of both anions.

**Registry No.** $H_3P_2O_8^-$, 58904-54-4; $Br^-$, 24959-67-9.

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# Inorganic Chemistry of Fluorocarbenes. 1. Reactions of Tetrafluoroethylidene with Fluorine-Containing Phosphines

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The interactions of tetrafluoroethylidene with three fluorine-containing phosphines have been investigated. The source of the carbene is the pyrolytic decomposition of $C_2F_5SiF_3$ at 200 °C. The reaction of $CF_3CF$ with $PF_3$ generates $CF_2{=}CFPF_4$ and $PF_5$; reaction with $(CF_3)_3P$ leads to $(CF_3)_2PCF(CF_3)_2$; and reaction with $(CF_3)_2PCF(CF_3)_2$ produces the fluorocarbon $(CF_3)_2CFCF(CF_3)_2$. The possibility that the vinylphosphorane product of the $PF_3$ reaction results from fluorine-transfer rearrangement of $C_2F_5PF_2$ as an intermediate product was discredited by a demonstration that $C_2F_5PF_2$ is thermally stable under the reaction conditions. Other mechanistic pathways are discussed.

## Introduction

The direct interaction of fluorocarbenes and volatile inorganic fluorides would seem to be a potentially valuable source of fluoroalkyl derivatives of the main-group elements. To date, however, such a synthetic approach has been severely impeded because of the remarkably low reactivity of $CF_2$—the most widely investigated fluorocarbene.[1] No reaction occurs between $CF_2$ and $NF_3$, $PF_3$, or $BF_3$.[2] One of the few inorganic fluorides known to react with $CF_2$ is $PF_5$; Mahler[2] has shown that several perfluoro(methylphosphoranes) are interconverted via reversible elision of $CF_2$

$$(CF_3)_xPF_{5-x} \rightleftharpoons CF_2 + (CF_3)_{x-1}PF_{6-x} \quad (x = 1\text{-}3)$$