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Kinetics of Self-decomposition of Peroxydiphosphate in Aqueous Sulphuric Acid Medium

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Kinetics of self-decomposition of peroxydiphosphate in aqueous sulphuric acid medium at $[H^+] = 0.2-1M$ and $\mu = 1.4M$ in the temperature range 40-70° has been investigated. The reaction is found to be first order each in [peroxydiphosphate] and $[H^+]$. H^+ is found to catalyse the reaction strongly. Effects of temperature, ionic strength and added HPO_4^{2-} on the reaction rate have been studied. Evidence for free radical intermediate is provided by the initiation of vinyl polymerization. IR spectrum of polyacrylonitrile formed by the initiation of peroxydiphosphate shows the presence of phosphate grouping. Kinetic and thermodynamic parameters, K_w (M^{-1} sec^{-1}), A, E_a, $\Delta S^{\ddagger}$, etc. have evaluated and discussed with suitable reaction mechanism. A critical comparison is also made with similar work involving peroxydisulphate.

AMONG the inorganic compounds containing peroxide bond, peroxydisulphate, $S_2O_8^{2-}$, is well-known with which extensive oxidation studies have been carried out[1,2]. But peroxydiphosphate (PP), $P_2O_8^{4-}$, which is isoelectronic and isostructural with the former, received relatively little attention and the oxidation studies involving the latter are very few in literature[3-8]. From the preparative method, the minimum value of the oxidation-reduction potential of $P_2O_8^{4-}$ was found to be −2.07 V (ref. 9, 10). Also the fact that it oxidizes vanadyl ions[5] and silver ions[11] indicates that the potential is not much different[7] from that of the peroxydisulphate couple which is −2.01 V. As a prelude to substrate oxidation and as an extension of our preliminary note[12], the results of self-decomposition of peroxydiphosphate are presented in this paper.

Materials and Methods

$K_4P_2O_8 \cdot 4H_2O$ (99.1%) was prepared from $K_4P_2O_8$ (FMC Corporation, USA) according to the method of Chulski[13]. H_2SO_4, $NaHSO_4$, ferrous ammonium sulphate, ceric ammonium sulphate and other chemicals used were of analar grade. Water used was doubly distilled over alkaline permanganate and deionized over Biodeminrolit (Permutit Co., UK) mixed-bed ion exchange resin.

All the experiments were carried out in aqueous sulphuric acid medium at $[H^+] = 0.2-1M$ and constant ionic strength of $1.4M$ (adjusted with $NaHSO_4$), with $[PP] = 5-30 \times 10^{-3}M$ in the temperature range 40-70°. $[H^+]$ always represents the absolute concentration of H^+, the dissociation of HSO_4^- and the alkalinity of peroxydiphosphate solution always being taken into consideration. The kinetics were followed by estimating the rate of disappearance of peroxydiphosphate, $-R_{PP}$, by adding a known excess concentration of Fe^{2+} (in $1N$ H_2SO_4) to the aliquots of the reaction mixture and estimating the unreacted Fe^{2+} by cerimetry using ferroin indicator.

Results and Discussion

A 2% solution of lithium peroxydiphosphate was found to have $pH \simeq 9.2$ and at this alkaline pH, peroxydiphosphate did not undergo any self-decomposition even at 80°. But the addition of small amounts of H^+ was found to catalyse the reaction strongly. The rate of disappearance of peroxydiphosphate, $-d[PP]/dt$ or $-R_{PP}$, obeyed second-order kinetics, first order each with respect to [PP] and $[H^+]$. Plots of $\log(a-x)$ vs time (min) where $(a-x) = [PP]_t$, were found to be linear only up to $\sim 15\%$ of the reaction and above that conversion, non-linearity was observed (Fig. 1). From the slopes of the straight line portion (initial slopes) of these semilogarithmic plots, pseudo-first-order rate constant, k', were evaluated.

$$k' (sec^{-1}) = slope \times 2.303/60$$

Plots of k' vs $[H^+]$ were found to be linear passing through the origin showing the dependence of rate on $[H^+]$ also to be of first order. $-R_{PP}$ vs [PP] plot which was linear passing through the origin and $\log(-R_{PP})$ vs $\log[PP]$ plot which was linear with a slope of unity, and the non-dependence of k' on the initial [PP] also confirmed the first-order dependence on [PP]. Hence the rate law for the self-decomposition of peroxydiphosphate or water oxidation by peroxydiphosphate can be given as

$$-\frac{d[PP]}{dt} = k_w[PP][H^+]$$

where k_w(M^{-1} sec^{-1}) is the second-order rate constant. The values of k_w ($\times 10^5$) evaluated at 40°, 50°, 60° and 70° and $\mu = 1.4M$ are 3.43, 6.52, 12.62 and 21.33 respectively.

Increase in ionic strength from 1.08 to 3.48M effected $\sim 50\%$ increase in the rate of disappearance
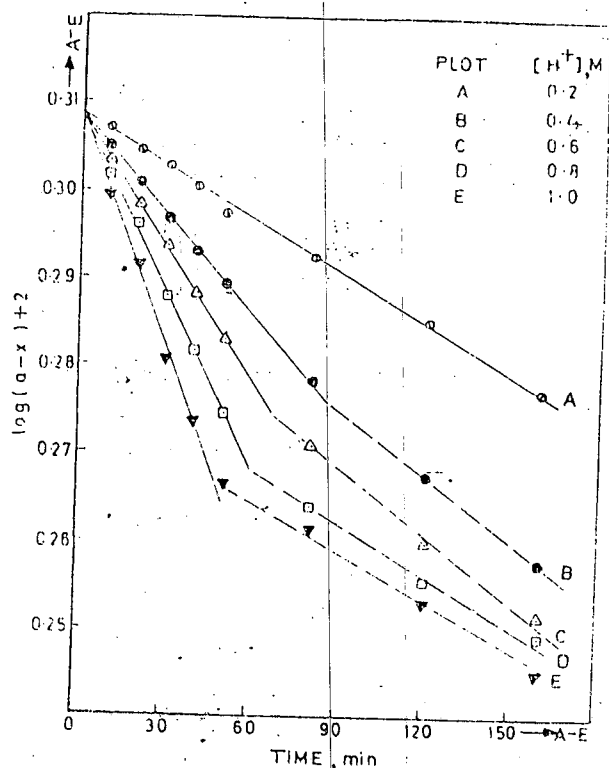
PLOT	$[H^+]$ M
A	0·2
B	0·4
C	0·6
D	0·8
E	1·0

Fig. 1 — Self-decomposition of PP at 40° [Plots showing the first-order dependence on PP (deviation at higher conversions is indicated in broken lines). [PP] = 0·02M, [H⁺] = 0·2-1·0M and μ = 1·4M]

of PP and the dependence of rate on ionic strength is in agreement with that expected for an ion-dipole reaction. It was suspected that the non-linearity of the semilogarithmic plots (Fig. 1) might be due to the inhibition by the product, PO_4^{3-}, formed. This was confirmed by the retardation of rate by initially added HPO_4^{2-} (Table 1).

Change in the nature of the cations of peroxydiphosphate did not affect the reaction rate, i.e. kinetic measurements with $Li_4P_2O_8 \cdot 4H_2O$ and $K_4P_2O_8$ gave rise to the same rate constants. Presence or absence of either atmospheric oxygen or light did not influence the reaction rate. Added acrylonitrile monomer was polymerized indicating the formation of free radicals as intermediates.

Acid catalysis and active species — It has been known for a long time that the rates of oxyanion reactions are markedly dependent on acid concentration[14-19]. It is presumed that the role of protons is to labilize oxygen by converting it from oxide ion to hydroxide ion and on to water. The addition of protons to oxide ion in an oxyanion should make it easier to break the bond. In oxidations involving

oxyanions, since covalent bonds to oxygen are generally broken simultaneously with electron transfer, they are found to be acid-catalysed. The reactions of peroxides are also subject to acid catalysis[21]. Hence it will not be surprising if the reactions of peroxydiphosphate which is both a peroxide and an oxyanion, i.e. oxyanion derivative of H-O-O-H, are subject to acid catalysis strongly. Peroxydiphosphate, $P_2O_8^{4-}$, is extensively protonated in acid medium due to the accumulation of high negative charge. The various species present are $P_2O_8^{4-}$, $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^{-}$ and $H_4P_2O_8$ and the concentration of these species varies drastically with change in pH (species involving the protonation of peroxidic oxygen, $H_5P_2O_8^+$, may also be present along with the other protonated species). The population of the different species as a function of pH is given by Crutchfield[22]. For example, the percentage contribution of each species to the total peroxydiphosphate concentration at $pH = 0$ ($1M H^+$) is $H_2P_2O_8^{2-}$, 16·7%; $H_3P_2O_8^-$, 55·5% and $H_4P_2O_8$, 27·8%. Under the present experimental conditions (0·2-1M H⁺) the pH is less than unity. From a knowledge of the concentrations of the various species, it is not possible to arrive at any definite conclusion about the nature of the active species. Usually, predictions about the nature of the active species are made on the basis of the dependence of the reaction rate on $[H^+]$. In the present study k' vs $[H^+]$ plots at all temperatures are found to be linear passing through origin showing a simple first-order dependence of the reaction rate on $[H^+]$. This will point to the singly protonated $HP_2O_8^{3-}$ as the active species. But at $pH < 1$, $HP_2O_8^{3-}$ does not exist and only higher protonated species are present. Hence even on the basis of the dependence of the reaction rate on $[H^+]$ it is not possible to predict the nature of the active species. The reaction rate as well as the concentration of $H_3P_2O_8^-$ and $H_4P_2O_8$ are increasing[22] with increase in $[H^+]$. Hence it is probable that one or both of these species may be active. Venturini et al.[23] suggested that in the region of $[H^+] = 0·01-0·7M$, only one kind of species, $H_3P_2O_8^-$ was responsible for the electrochemical reduction of peroxydiphosphate and it is likely that under the present experimental condition also, $H_3P_2O_8^-$ is the active species.
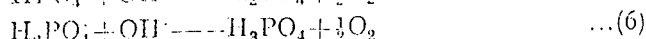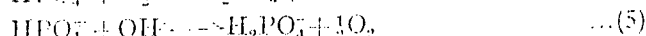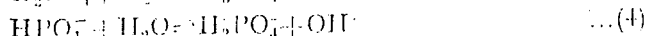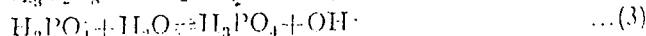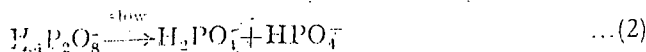
Free radicals as intermediates — IR spectrum of polyacrylonitrile formed by the initiation of peroxydiphosphate, showed peaks corresponding to P-O stretching frequencies indicating the presence of phosphate grouping in the polymer. Hence it may be concluded that PO_4^{2-} (HPO_4^- or H_2PO_4) radical ions are produced as intermediates. Formation of PO_4^{2-} was suggested earlier by Edwards and coworkers[5-8] in the thermal oxidation of VO^{2+} and Fe(II) complexes and photochemical oxidation of water, ethanol and 2-propanol by peroxydiphosphate. Peroxydiphosphate is a two-electron oxidizing agent. The formation of free radicals as intermediates in oxidation studies involving peroxydiphosphate evidently indicates that it functions as a one-electron oxidant.

TABLE 1 — EFFECT OF ADDED Na_2HPO_4 ON RATE

[PP] = $2·05 \times 10^{-2}M$; [H⁺] = 0·4M; μ = 1·4M; Temp. = 60°]

$[Na_2HPO_4]$, M	—	0·1	0·2	0·3	0·4
$-R_{PP} \times 10^7$, (mole litre⁻¹ sec⁻¹)	9·52	5·60	3·02	1·03	0·41

Mechanism and rate law — On the basis of the above experimental observations and in analogy with the mechanism proposed for the photochemical oxidation of water[6] by peroxydiphosphate, the following mechanism may be proposed:-
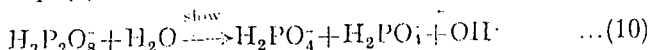
$$H_2P_2O_8^{2-} + H^+ \overset{K_{14}}{\rightleftharpoons} H_3P_2O_8^- \qquad \ldots(1)$$

$$H_3P_2O_8^- \overset{slow}{\longrightarrow} H_2PO_4^- + HPO_4^- \qquad \ldots(2)$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH \cdot \qquad \ldots(3)$$

$$HPO_4^- + H_2O \rightleftharpoons H_2PO_4^- + OH \cdot \qquad \ldots(4)$$

$$HPO_4^- + OH \cdot \longrightarrow H_2PO_4^- + \tfrac{1}{2}O_2 \qquad \ldots(5)$$

$$H_2PO_4^- + OH \cdot \longrightarrow H_3PO_4 + \tfrac{1}{2}O_2 \qquad \ldots(6)$$

Reactions of the type

$$2OH \cdot \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad \ldots(7)$$

$$2HPO_4^- \longrightarrow H_2P_2O_8^{2-} \qquad \ldots(8)$$

and

$$2H_2PO_4^- \longrightarrow H_4P_2O_8 \qquad \ldots(9)$$

are also probable in the above mechanism. The reactions (3) and (4) appear to reach equilibrium under all experimental conditions since added HPO$_4^{2-}$ inhibits the reaction very much (Table 1). One cannot rule out the possibility of H$_3$PO$_5$ being formed under the present experimental condition by hydrolysis[22] and also by the combination of H$_2$PO$_4^-$ and OH·. The initiation step given by Eq. (2) may also be replaced by Eq. (10)

$$H_3P_2O_8^- + H_2O \overset{slow}{\longrightarrow} H_2PO_4^- + H_2PO_4^- + OH \cdot \qquad \ldots(10)$$

From the experimental results it is not possible to differentiate between the two types of initiation, i.e. steps (2) and (10), as in the case of peroxydisulphate[1,2].

Since $[PP]_{Total} = [H_2P_2O_8^{2-}] + [H_3P_2O_8^-] + [H_4P_2O_8]$ under the present experimental conditions, the rate law for the decomposition of PP, in accordance with the above mechanism with H$_3$P$_2$O$_8^-$ as the active species, can be given as

$$\frac{-d[PP]}{dt} = k[H_3P_2O_8^-] = \frac{kK_{13}[PP]_T[H^+]}{1 + K_{13}[H^+] + K_{13}K_{14}[H^+]^2} \qquad \ldots(11)$$

where K_{13} and K_{14} are the equilibrium constants for the protonation of H$_2$P$_2$O$_8^{2-}$ and H$_3$P$_2$O$_8^-$ respectively. The experimentally observed first order dependence of rate on [H$^+$] is incompatible with the above rate law. Hence it might appear that H$_3$P$_2$O$_8^-$ may not be the active species. Such a simple first order dependence of rate on [H$^+$] was observed in the electrochemical reduction[23] of PP wherein H$_3$P$_2$O$_8^-$ was concluded to be the active species. We have also encountered similar first order dependence of rate on [H$^+$] in the oxidations of a number of substrates[20] by PP, with H$_3$P$_2$O$_8^-$ as the active species, decomposition of PP being the rate-determining step and the order with respect to substrate being zero. The rate law derived theoretically (Eq. 11) would be reduced to the one observed experimentally as

$$\frac{-d[PP]}{dt} = kK_{13}[PP]_T[H^+] = k_w[PP]_T[H^+] \qquad \ldots(12)$$

only when the second and third terms of the denominator of Eq. (11) are negligible compared to unity, the first term. $K_{13} \simeq 3.3$ and $K_{14} \simeq 0.5$ according to Crutchfield and Edwards[27] and hence such a simplification of the rate law (11) may not be possible. But the authors[27] themselves had pointed out that the first and second dissociations of H$_4$P$_2$O$_8$ were so strong that inflection points were not observed in the pH titration curve and the approximate values of K_1 and K_2 ($K_{13} = 1/K_2$ and $K_{14} = 1/K_1$) were estimated from the trend observed in other tetravalent acids of similar structure. The uncertainty in the values of K_1 and K_2 (hence K_{13} and K_{14}) reported[27] was also stressed by Venturini et al.[28] who claimed that K_1 and K_2 should be very much greater than the reported values. Hence K_{13} and K_{14} values would be very much less and consequently it would not be unreasonable if we assume that $K_{13}[H^+] + K_{13}K_{14}[H^+]^2$ can be neglected compared to unity (Eq. 11) leading to the simplified rate law (Eq. 12) which explains the experimentally observed order with respect to [H$^+$].

Kinetic constants — The apparent energy of activation, E_a (kcal/mole) and the frequency factor, $A(M^{-1}$ sec^{-1}) evaluated by the method of least-squares may be expressed in the form of Arrhenius equation:

$$k_w(M^{-1}sec^{-1}) = (5.01 \pm 0.05) \times 10^4 \exp[-(13.13 \pm 0.19)/RT] \qquad \ldots(13)$$

The low value of the frequency factor A ($5.01 \times 10^4 M^{-1}$ sec^{-1}) and hence the low value of the steric factor, P ($\sim10^{-7}$ to 10^{-8}) may be explained in terms of the statistical theory as follows. P may be identified approximately with the quantity $(f_v/f_R)^5$ for a reaction involving two polyatomic molecules, where f_V and f_R are vibrational and rotational

TABLE 2 — COMPARISON WITH S$_2$O$_8^{2-}$

	Peroxydiphosphate	Peroxydisulphate[1,2,25]
1.	Reaction occurs only in acid medium at ordinary temperatures	Reaction occurs both in alkaline and acid media
2.	Acid catalysed	Acid-catalysed
3.	Rate law: $-\dfrac{d[PP]}{dt} = k_w[PP]_T[H^+]$	Rate law: $-\dfrac{d[S_2O_8^{2-}]}{dt} = k_0[S_2O_8^{2-}]$ (at constant [H$^+$]) $= k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][H^+]$
4.	Acid-dependent path only	Both acid-dependent and acid-independent paths
5.	At 50°, 0.5M H$^+$ and $\mu = $ 1.4M, the overall rate constant, $k_w[H^+] = 3.26 \times 10^{-5}$ sec^{-1}	At 50°, 0.5M H$^+$ and $\mu = $ 0.5M, the overall rate constant, $k_0 = 2.5 \times 10^{-5}$ sec^{-1} (or 1.5 $\times 10^{-3}$ min^{-1})
6.	$E_a = 13.13$ kcal/mole	$E_a = 33.5$ kcal/mole for acid-independent k_1-path and $E_a = 26$ kcal/mole for acid dependent k_2-path
7.	Free-radical chain mechanism is operative	Free radical chain mechanism is operative
8.	Oxidation occurs by one-electron route	Oxidation occurs by one-electron route

partition functions respectively. At ordinary temperatures f_V is generally of the order of unity and f_R is of the order of 10 to 100. Hence the probability factor will be about 10^{-5} to 10^{-10}. The large negative value of entropy of activation, $\Delta S^{\ddagger} = 39.22$ e.u., may also account for the low value of P and hence the frequency factor. The peroxide bond, $-O-O-$, is associated with the bond energy[24] of 33.2 kcal/mole and the reactions involving the homolytic scission of peroxide bond may be expected to have activation energies of this magnitude. For the homogeneous decomposition proceeding by homolytic $-O-O-$ bond fission in either the gas phase or liquid phase, a number of peroxides[25] such as diethyl peroxide, dibenzoyl peroxide, di-t-butyl peroxide, cumene hydroperoxide and peroxydisulphate exhibit activation energies of about 30-40 kcal/mole. But the self-decomposition of peroxydiphosphate is found to have $E_a = 13.13$ kcal/mole which is very much striking. This may be due to the strong protonation (also of peroxidic oxygen) and solvation of peroxydiphosphate which render the peroxide bond much weaker. In the case of oxidation by peroxydisulphate[26], the activation energy for the acid-catalysed path involving $HS_2O_8^-$ as the active species was found to be 26 kcal/mole. For the uncatalysed reaction with $S_2O_8^{2-}$ as the active species, the energy of activation was found to be 33.5 kcal/mole. The decrease in the activation energy by 7.5 kcal/mole may be ascribed to the protonation of $S_2O_8^{2-}$. In the case of peroxydiphosphate, the very low value of E_a may be explained on the same grounds. Moreover E_a represents the overall activation energy and hence the correlation of E_a with the cleavage of a single bond is difficult.

Comparison with $S_2O_8^{2-}$ — It is also of interest to compare the self-decomposition of the two peroxyanions, peroxydiphosphate and peroxydisulphate. The points of similarity and difference between the reactions of the two oxidants with water are outlined in brief in Table 2.

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