Oxidation of Benzaldehydes by Peroxomonophosphoric Acid. A Kinetic and Mechanistic Study in Acid and Alkaline Media

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The oxidation of benzaldehydes by peroxomonophosphoric acid has been found to proceed by

(i) $-d[\text{peroxomonophosphoric acid}]/dt \propto [\text{benzaldehyde}][\text{peroxomonophosphoric acid}][H^+]^x$

where x=a fraction at $[H^+] < 0.5$ M and $x=0$ at $[H^+] > 0.5$ M and

(ii) $-d[\text{peroxomonophosphate}]/dt \propto [\text{benzaldehyde}][\text{peroxomonophosphate}][OH^-]^y$

where y=a fraction at $[OH^-] < 0.1$ M and $y=0$ at $[OH^-] > 0.1$ M.

In the alkaline oxidation Hammett relationship is obeyed excellently, unlike the oxidation in the acid medium. The oxidation mechanisms are discussed in terms of a nucleophilic attack of the peroxomonophosphoric acid species on the carbonyl carbon centre. Thermodynamic parameters have been evaluated to substantiate the mechanisms.

Peroxomonophosphoric acid (PMPA) is known to function through a polar mechanism in spite of the fact that these compounds are sources of free radicals due to homolysis of O–O bonds not only in homogeneous media but also in some heterogeneous reactions.[1–3] Operation of a polar mechanism in oxidations by peroxo compounds was first recognised by Swern.[4] Kinetics of oxidation of halide ions[5] by peroxomonophosphoric acid, peroxomonosulfuric acid and peracetic acid, and of iodide ion[6] by peroxomonophosphoric acid involve both H^+-dependent and H^+-independent terms.

A survey of literature, however, reveals that studies relating to PMPA oxidation of organic substrates are quite few. Hence it was thought worthwhile to investigate the possibility of the use of PMPA as an oxidant for organic substrates. More interesting is the use of PMPA in alkaline medium which is probably for the first time we have attempted to undertake. This report deals with the kinetics of oxidation of aromatic aldehydes by PMPA in acid and alkaline media.

Experimental

All the chemicals used were of Analar grade. Benzaldehydes used were freshly distilled or recrystallized samples. PMPA was prepared by the acid hydrolysis[5–7] of $K_4P_2O_8$. The acidity of the medium was adjusted with $HClO_4$ or H_2SO_4 as the case may be and the ionic strength of the medium was maintained by adding requisite amounts of $NaClO_4$ or $NaHSO_4$. In the case of experiments in alkaline medium, the acid after hydrolysis of peroxodiphosphate was first neutralised by adding a calculated amount of alkali and then a known excess of alkali was added so as to obtain the required hydroxide concentration. Reactions were followed by measuring the rate of disappearance of PMPA, the estimation of which was done in an acetic acid–acetate buffer of pH 4—5 by the usual iodometric procedure. In separate experiments, the oxidation rates followed by the disappearance of PMPA were found to check within 2—6% with the rates followed by measuring the formation of benzoic acid spectrophotometrically. The self decomposition of the oxidant was routinely checked and found to be either nil or negligibly small under our experimental conditions. The aerial oxidation of benzaldehyde was found to be negligible because the rates of oxidation in an atmosphere of nitrogen, in representative runs, agreed with in 3—5% to those in the presence of air.[8,9]

Results and Discussion

Reactions in Acid Medium. *Stoichiometry*: Experiments conducted with excess of PMPA, in the presence of air or under a nitrogen atmosphere, showed that the stoichiometry of aldehyde to PMPA is 1: 1 and the product is the corresponding benzoic acid.

Benzaldehyde has been oxidised by PMPA in aqueous medium in the presence of $HClO_4$ and H_2SO_4 at 35 °C at constant ionic strength. The reaction is found to be first order with respect to the disappearance of PMPA and to the substrate (Table 1).

Dependence on $[H^+]$: The variation of $[H^+]$ ($HClO_4$ or H_2SO_4) is accompanied by a variation of rate in the same direction suggesting the reaction to be acid-catalysed. However, this catalysis is observed upto $H^+=0.5$ M beyond which the rate tends to become independent of the acid concentration.

Effect of Added Substances: A change in the ionic strength of the medium or the addition of acrylamide or Cu^{2+} does not affect the oxidation rate. The decrease in the rate in the presence of HPO_4^{2-} may be due to the removal of H^+ from the reaction medium (Table 1).

Effect of Substituents: The second order rate constants (k_2') for the oxidation of benzaldehydes are summarised in Table 2. It is interesting to note that the substituent effect on the reaction rate is insignificant in acid medium; the electron-withdrawing *p*-nitro substituent and the electron-releasing *p*-methyl substituent only marginally influence the rate whereas the other substituents are without any effect. Such observations on anomalous substituent effect have been reported earlier.[10,10a)] It might have arisen because of the operation of a preliminary hydration equilibrium,[10a)]

$$XC_6H_4CHO + H_2O \overset{K_p}{\rightleftharpoons} XC_6H_4CH(OH)_2,$$

competing with the oxidation steps; an electron withdrawing *p*-nitro substituent would favour the formation of the hydrate, but would retard the oxidation process because of a fall in the effective concentration of benzaldehyde available for oxidation (benzaldehyde is prefered to the hydrate in the oxidation steps because otherwise the substituent effects would have been in the same direction; *e.g.*, an electron-withdrawing substituent would have enhanced the rate and an electron-releasing substituent would have retarded it).

TABLE 1.[a] OXIDATION OF BENZALDEHYDES BY PMPA IN ACID MEDIUM

Substrate (S)	$\frac{10^3\,S}{M}$	$\frac{10^3\,PMPA}{M}$	$\frac{HClO_4}{M}$	HOAc–Water (% v/v)	$\frac{10^2\,k_2'}{dm^3\,mol^{-1}\,s^{-1}}$
Benzaldehyde	5.29	4.27	0.1	20—80	0.62
	5.31	8.60	0.1		0.63
	5.31	6.42	0.1		0.66
	2.74	4.16	0.3		1.90
	5.11	4.28	0.3		1.66
	10.63	4.16	0.3		1.76
	25.56	4.16	0.3		1.83
	5.29	4.17	0.3	30—70	1.61
	5.26	0.64	0.05	Aqueous	0.59 (1.07)[b]
	5.43	4.56	0.1		0.94 (1.5)
	5.26	0.57	0.2		1.43 (2.0)
	5.14	4.27	0.3		2.02 (2.2) 1.89[c]
	5.14	4.34	0.3		1.78[d]
	5.43	4.38	0.5		2.56 (2.42)
	5.27	1.14	0.75		2.64 (2.53)
	5.37	0.59	0.5[e]		3.6
	5.23	1.08	0.5[e]		3.48
	5.21	4.07	0.5[e]		3.63
	2.46	4.41	0.5[e]		4.75
	5.29	4.41	0.5[e]		3.66
	10.52	4.41	0.5[e]		3.70
p-Nitrobenzaldehyde	2.07	0.59	0.05		1.20 (1.27)
	2.09	1.10	0.1		1.50 (1.83)
	2.07	0.60	0.2		2.32 (2.35)
	2.13	1.19	0.3		2.58 (2.60)

a) At I=1.5 M and 35 °C. b) (In parentheses) $10^2\,k_2'$ calcd $dm^3\,mol^{-1}\,s^{-1}$. c) Rate of formation of benzoic acid. d) In the presence of added HPO_4^{2-} (5.02×10^{-2} M). e) At 0.5 M H_2SO_4.

TABLE 2.[a] OXIDATION OF BENZALDEHYDES BY PMPA: EFFECT OF SUBSTITUENTS

Substrate	$\frac{10^2\,k_2'\,^{b)}}{dm^3\,mol^{-1}\,s^{-1}}$	$\frac{10^2\,k_2'\,^{c)}}{dm^3\,mol^{-1}\,s^{-1}}$	$\frac{10^2\,k_2''\,^{d)}}{dm^3\,mol^{-1}\,s^{-1}}$
Benzaldehyde(H–)	1.66	2.95	7.30
p-Nitro-	2.33	4.15	63.56
m-Nitro-	1.75	2.91	58.26
p-Chloro-	1.61	2.51	15.45
m-Chloro-	—	—	22.05
o-Chloro-	—	—	6.93
p-Bromo-	1.68	2.56	18.31
m-Bromo-	—	—	22.55
p-Methyl-	3.03	5.15	3.81
p-Methoxy-	1.78	—	2.48

a) At 35 °C. b) $HClO_4$, 0.3 M; HOAc: water, 20:80; I=0.5 M. c) H_2SO_4, 0.5 M; HOAc: water 20:80; I=2.0 M. d) OH^-, 0.2 M; aqueous medium, I=0.5 M.

Solvent Effect: The oxidation rate is found to decrease marginally with increase in acetic acid content in the solvent mixture (Table 1). The marginal decrease in the rate with decrease in dielectric constant of the medium is to be expected for a reaction involving a neutral molecule and an ion[11] to which the present reactions probably conform.

Rate Law: The various equilibria involving PMPA in the solution are

$$H_3PO_5 \overset{K_1}{\rightleftarrows} H_2PO_5^- + H^+, \tag{1}$$

$$H_2PO_5^- \overset{K_2}{\rightleftarrows} HPO_5^{2-} + H^+, \tag{2}$$

$$HPO_5^{2-} \overset{K_3}{\rightleftarrows} PO_5^{3-} + H^+. \tag{3}$$

K_1, K_2, and K_3 values are 8.0×10^{-2}, 4.2×10^{-6}, and 1.6×10^{-13} respectively at 25 °C.[7] Since in the [H⁺] range used, PMPA exists[7] as H_3PO_5 and $H_2PO_5^-$, the oxidation steps may be written as

$$XC_6H_4CHO + H_2O \overset{K_p}{\rightleftarrows} XC_6H_4CH(OH)_2, \tag{A}$$

$$H_2PO_5^- + H^+ \overset{K}{\rightleftarrows} H_3PO_5, \tag{4}$$

$$H_2PO_5^- + XC_6H_4CHO \xrightarrow{k_1} XC_6H_4COOH + H_2PO_4^-, \tag{5}$$

and

$$H_3PO_5 + XC_6H_4CHO \xrightarrow{k_2} XC_6H_4COOH + H_3PO_4. \tag{6}$$

The reaction sequence leads to the rate law

$$-\frac{d[PMPA]}{dt} = [PMPA][XC_6H_4CHO]\left\{\frac{k_1+k_2K[H^+]}{1+K[H^+]}\right\} \times (1+K_p[H_2O]), \tag{7}$$

where

$$k_2' = \left\{\frac{k_1+k_2K[H^+]}{1+K[H^+]}\right\}(1+K_p[H_2O]). \tag{8}$$

Since $1/K_1=K$, and $K_p[H_2O]\ll1$,[15] Eq. 8 becomes

$$k_2' = \frac{K_1k_1+k_2[H^+]}{K_1+[H^+]}. \tag{9}$$

This rate law (Eq. 9) is in agreement with the experimental findings. The values of k_1 and k_2 have been calculated by the method of least squares from Eq. 9. The values of k_2 for benzaldehyde and *p*-nitrobenzaldehyde are 2.80×10^{-2} and 3.29×10^{-2} $dm^3\,mol^{-1}\,s^{-1}$ respectively. For both the compounds, the values of k_1 are small and negative and thus can be approximated to zero. Therefore the Eq. 9 reduces to

$$k_2' = \frac{k_2[H^+]}{K_1+[H^+]}. \tag{10}$$

The rate constants (k_2' calcd) as obtained from Eq. 10 at different [H⁺] are recorded in Table 1. It appears that in the lower [H⁺], k_2' calcd values for benzaldehyde are significantly higher than the experimental ones (k_2') and this can probably be ascribed to the contribution of the k_1 term at lower [H⁺] to the observed k_2' as defined by Eq. 9. It is now evident that the species H_3PO_5 is important in the reaction. It is also natural

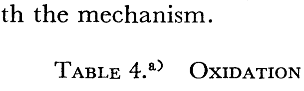
Table 3.a) Oxidation of benzaldehydes by PMP in alkaline medium

Substrate (S)	$\frac{10^3\ \mathrm{S}}{\mathrm{M}}$	$\frac{10^4\ \mathrm{PMP}}{\mathrm{M}}$	$\frac{\mathrm{OH}^-}{\mathrm{M}}$	I/M	$\frac{10^2\ k_2''}{\mathrm{dm^3\ mol^{-1}\ s^{-1}}}$
Benzaldehyde	2.80	5.37	0.204	0.5	7.30
	5.38	5.37	0.204	0.5	7.60
					7.45b)
	10.27	4.85	0.205	0.5	7.83
	24.98	5.57	0.204	0.5	7.28
	9.98	4.66	0.050	0.1	1.95
	10.41	5.03	0.05	0.302	2.88
	9.72	5.01	0.05	0.503	3.41
	10.06	3.94	0.017	0.5	1.40
	10.06	4.33	0.031	0.5	2.43
	10.22	4.11	0.105	0.5	5.95
	2.61	4.74	pH 10	—	0.52
p-Nitrobenzaldehyde	2.62	3.80	0.019	0.5	29.15 (30.52)c)
	2.62	3.91	0.0387	0.5	46.21 (44.79)
	2.61	4.24	0.058	0.5	55.73 (54.25)
	2.61	4.56	0.098	0.5	65.08 (66.61)

a) At 35 °C in aqueous medium. b) Rate of formation of benzoate ion. c) (In parentheses) $10^2\ k_2''$ calcd dm^3 mol^{-1} s^{-1}.

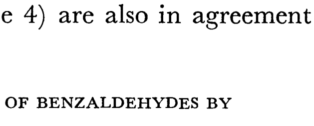
to expect a very insignificant value of k_1, since in the range of [H$^+$] used, PMPA would mainly exist as H_3PO_5.[7)]

Peroxo compounds are known to act as nucleophiles since the peroxo group can attach itself to a reactive site (*i.e.*, a p-orbital of carbon). Thus the peroxomonophosphoric acid can attack the carbonyl carbon of the aldehyde giving rise to transition state of the form:



$$\left[\mathrm{XC_6H_4\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\vdots}}{C}}\cdots\overset{\overset{\displaystyle H}{|}}{O}\text{-}O\text{-}PO_3H_2}\right]$$

(I)



$$\left[\mathrm{XC_6H_4\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{\vdots}}{C}}\cdots\overset{\overset{\displaystyle H}{|}}{O}\text{-}O\text{-}PO_3H}\right]^-$$

(II)

This is consistent with the idea of Edwards[12)] that in the reactions of peroxo compounds with inorganic and organic substrates, a fair degree of covalent bonding developes between the redox pair. The activation parameters calculated (Table 4) are also in agreement with the mechanism.

Table 4.a) Oxidation of benzaldehydes by PMP: thermodynamic parameters

Substrate	$\frac{\Delta H^{\neq\,\mathrm{b)}}}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta S^{\neq\,\mathrm{b)}}}{\mathrm{J\ mol^{-1}\ K^{-1}}}$	$\frac{\Delta H^{\neq\,\mathrm{c)}}}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta S^{\neq\,\mathrm{c)}}}{\mathrm{J\ mol^{-1}\ K^{-1}}}$
Benzaldehyde(H–)	39.4	−145.3	35.8	−150.6
p-Nitro-	33.4	−161.4	48.6	− 91.0
p-Methyl-	33.4	−160.5	35.8	−156.1
p-Methoxy-	32.3	−163.7	—	—

a) Calculated at 298 K. b) H_2SO_4, 0.5 M; aqueous medium, I=1.5 M. c) OH$^-$, 0.2 M, aqueous medium, I=0.5 M.

Reactions in the Alkaline Medium: The oxidation of benzaldehydes by peroxomonophosphate (PMP) in alkaline medium follows a first order dependence each on oxidant and substrate as shown by the constancy of the pseudo first order rate constants (k_1'') upto a high percentage of the reaction in any single run and the constancy of $k_1''/[\mathrm{S}]$ ($=k_2''$) values respectively. The dependence of rate on [OH$^-$] is peculiar; the rate increases with an increase in the [OH$^-$] at lower [OH$^-$] and tends to reach a limiting value at higher [OH$^-$] (Table 3).

Substituent Effect: Substituent effect in alkaline medium is another important observation made which is kinetically different from that in acid medium. The substituents manifest their influence implying electronic effects are prominent for the oxidation in alkaline medium. The rate variation is essentially in agreement with the Hammett's substituent constants, σ (Table 2); a plot of log k_2'' *vs.* σ is linear (r=0.992) with a positive slope (ρ=1.27), which is indicative of a developing negative charge in the side chain of the benzaldehyde molecule.[13)] The magnitude of the ρ value is close to that observed for the ionization of benzoic acids (ρ=1.0).

Effect of Temperature: Identical enthalpy and entropy of activation observed for benzaldehyde and the *p*-methyl derivative (Table 4) suggest that oxidation of both the compounds are isoentropic; however, *p*-nitro derivative requires higher energy of activation and much higher entropy of activation compared to the other two derivatives, inspite of the higher reactivity of the *p*-nitro derivative. This is probably due to the reason that a greater concentration of *p*-nitrobenzaldehyde will be available in the hydrate form compared to that for benzaldehyde or *p*-methylbenzaldehyde.

Rate Law and Mechanism: At pH>11, peroxomonophosphate exists[7)] as HPO_5^{2-} and PO_5^{3-}.

$$\mathrm{HPO_5^{2-} + OH^- \xrightleftharpoons{K_4} PO_5^{3-} + H_2O} \qquad (11)$$

In alkaline medium benzaldehydes also exist[15,16)] in the hydrated form because of the following equilibria:

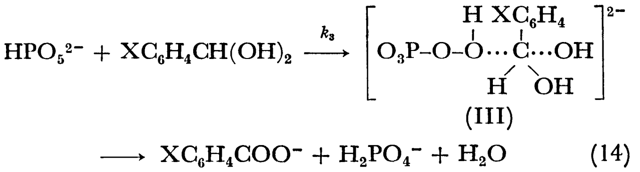
$$\mathrm{XC_6H_4CHO + OH^- \xrightleftharpoons{K_5} XC_6H_4CH(OH)O^-}, \qquad (12)$$

$$\mathrm{XC_6H_4CH(OH)O^- + H_2O \xrightleftharpoons{K_6} XC_6H_4CH(OH)_2 + OH^-}. \qquad (13)$$

Even though the equilibrium (13) has been considered to be unimportant by earlier workers;[16)] Sayer,[14)] and Bell and Sorensen[15)] attach significance to this equilibrium and have evaluated the formation constant for $XC_6H_4CH(OH)_2$. An examination of the formation constants though reveals the predominance of $XC_6H_4CH(OH)O^-$, $XC_6H_4CH(OH)_2$ is considered to be the reactive species in this oxidation process. This arises mainly from the following reasons (i) that the OH$^-$-dependence would have been more than unity had the reacting species been the hydrate mono anion because of the participation of OH$^-$ in steps (Eqs. 11 and 12), (ii) that there would have been a marked ionic strength effect if the reaction involved two ions. The marginal effect of ionic strength on rate points the reaction to involve at least one neutral molecule[17)] and

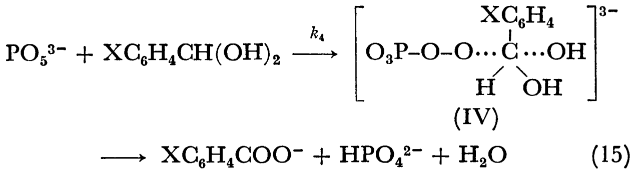
(iii) that the attack of the PMP species on the more electrophilic $XC_6H_4CH(OH)_2$ will be favoured.

So the reaction would involve a nucleophilic attack of the peroxo di- and tri-anions on the carbonyl carbon of the aldehyde hydrate molecule giving rise to the transition states III and IV respectively. The thermodynamic parameters calculated are in the range expected for a bimolecular substitution reaction.



$$HPO_5^{2-} + XC_6H_4CH(OH)_2 \xrightarrow{k_3} \left[O_3P\text{-}O\text{-}\overset{H}{O}\cdots\overset{XC_6H_4}{C}(H)(OH)\cdots OH \right]^{2-} \longrightarrow XC_6H_4COO^- + H_2PO_4^- + H_2O \qquad (14)$$

(III)



$$PO_5^{3-} + XC_6H_4CH(OH)_2 \xrightarrow{k_4} \left[O_3P\text{-}O\text{-}O\cdots\overset{XC_6H_4}{C}(H)(OH)\cdots OH \right]^{3-} \longrightarrow XC_6H_4COO^- + HPO_4^{2-} + H_2O \qquad (15)$$

(IV)

On the basis of the proposed mechanism the rate law can be derived as:

$$-\frac{d[PMP]}{dt} = \left\{\frac{k_3K_hK_5K_6+k_4K_5K_6[OH^-]}{K_h+[OH^-]}\right\} \times [PMP][XC_6H_4CHO], \qquad (16)$$

where

$$k_2'' = \frac{k_3K_hK_5K_6+k_4K_5K_6[OH^-]}{K_h+[OH^-]} \qquad (17)$$

and

$$\frac{K_4}{[H_2O]} = \frac{1}{K_h}.$$ ($K_h=K_w/K_3$, where K_w is the ionic product of water and K_3 is the dissociation constant of HPO_5^{2-})

Rearrangement of Eq. 17 would give

$$k_2''(K_h+[OH^-]) = k_3K_hK_5K_6 + k_4K_5K_6[OH^-]. \qquad (18)$$

On plotting $k_2''(K_h+[OH^-])$ against $[OH^-]$, linearity ($r=0.99$) is observed for both benzaldehyde and *p*-nitrobenzaldehyde.

From the intercept and slope of the plot, and employing the reported K_5 and K_6 values,[15] the values of k_3 and k_4 for *p*-nitrobenzaldehyde are calculated to be 0.34 $dm^3 mol^{-1} s^{-1}$ and 6.76 $dm^3 mol^{-1} s^{-1}$ respectively. The higher k_4 value is quite in agreement with the higher nucleophilic reactivity of PO_5^{3-} in alkaline medium. With these k_3 and k_4 values, the rate constants k_2'' (calcd) from Eq. 17 are collected in Table 3. In the case of benzaldehyde, since the least squares plot results in a very small and negative intercept, the value of k_3 is approximated to zero. The value of $k_4K_5K_6$, as given by the slope is 1.07×10^{-1}. The value of k_4 for benzaldehyde could not be calculated because of the non-availability of the K_5 and K_6 values.

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