Peroxomonophosphoric Acid Oxidations: Kinetics and Mechanism of Oxidation of Aliphatic Aldehydes

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The peroxomonophosphoric acid (PMPA) oxidation of six aliphatic aldehydes has been studied in the pH range 0—13. The reactions are second order, first order each in [aldehyde] and [PMPA] at constant pH. In alkaline medium the stoicheiometric ratio of PMPA to aldehyde is 1.0. In acid medium the ratio is significantly higher (1.5) pointing to the fact that an oxidation reaction and a carbonyl-assisted decomposition of PMPA occur simultaneously through a common intermediate. The pH–rate dependence was complex. A suitable rate law in a limited pH range 0—3 has been derived.

We have been recently interested in the oxidation of aromatic amines [1-3] by peroxomonophosphoric acid (PMPA). Our kinetic and product studies could be best interpreted in terms of an S_N2 transition state in which the amine lone pair initiated a nucleophilic attack on the electrophilic peroxo bond. H_3PO_5 is a unique peracid in which the ionised species $H_2PO_5^-$, HPO_5^{2-}, and PO_5^{3-} are in the decreasing order of electrophilicity. The other mechanistic extreme of nucleophilic attack by peroxoanion at electrophilic carbon [4,5] and sulphur [6] centres is possible. The ready oxidation of benzaldehyde [6] in alkaline medium is one such case, which involved rate-limiting H^- loss. The oxidation of benzaldehyde, hydroxybenzaldehydes, and *p*-methoxybenzaldehyde in acidic medium presented a situation where aryl migration was competing with hydride loss.[5] Thus structural and electronic effects could not be clearly discerned in view of the multiplicity of the pathways occurring simultaneously. We felt that better insight into aldehyde oxidation by PMPA could be obtained in the case of aliphatic aldehydes, where there is no possibility of Baeyer–Villiger oxidation. We present our results on the oxidation of series of aliphatic aldehydes where, fortunately, quantitative estimates of hydration equilibria are available.[7]

Results and Discussion

The reactions are overall of second order, first order in both [PMPA] and [aldehyde] at constant acidity. Plots of log titre *versus* time are linear till at least three half lives. The pseudo-first-order rate constants for the disappearance of PMPA (k_1'/s^{-1}) are nearly constant for a 15-fold variation in the initial [PMPA] (Table 1). Thus the first-order dependence on PMPA is established. Rate data in Table 2 show that there is unit dependence on the aldehyde. The simplest rate expression at any given pH can be written as (1).

$$\text{Rate} = k_{2}'_{(\text{obs})}\,[\text{PMPA}][\text{Aldehyde}] \qquad (1)$$

pH Dependence.—The kinetics of oxidation of formaldehyde and propionaldehyde have been studied in the pH range 0—13 and the data are collected in Tables 3 and 4. The reactions are fastest in strongly acidic and alkaline media. In the intermediate pH range 3—8 a bell-shaped curve is observed with a peak centred around pH 5.0—5.3. Acid catalysis in peroxidic reactions is mainly due to the predominance of the highly reactive electrophilic species H_3PO_5. The rapid increase in rate above pH 10 is a pointer to a different mechanism, *i.e.* nucleophilic attack at the carbonyl carbon by the peroxoanion PO_5^{3-} which is generated by the ionisation of the $^-O^-O^-H$ group (pK_3 of PMPA [8] is 12.8).

In the pH range 0—3, the steps in the Scheme are envisaged. This leads to the rate expression (2). The reactivities of

$$k_{2}'_{(\text{obs})} = (k_1[H^+] + k_2K_1)/(K_1 + [H^+]) \qquad (2)$$

Table 1. Dependence of rate of oxidation on [PMPA] [a]

10^3[PMPA]/M	$10^4k_1'$/s^{-1}
1.05	44.0
1.78	41.2
3.78	43.5
7.51	43.2
15.10	44.2

[a] $[H^+]$ 0.5M, [Propionaldehyde] 0.052M, 35 °C, aqueous medium.

Table 2. Substrate dependence in the PMPA oxidation of aliphatic aldehydes [a]

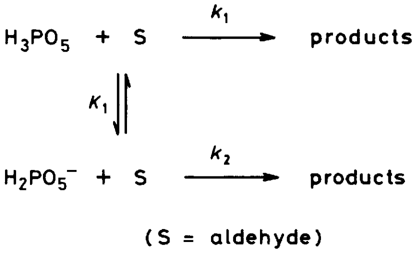
[Acetaldehyde]/M	$10^4k_1'$/s^{-1}	k_2'/l mol^{-1} s^{-1}
0.0073	6.10	0.084
0.0098	13.6	0.138
0.0105	12.8	0.122
0.0215	23.5	0.109
0.041	39.1	0.095
	(Average k_2' 0.11)	
[Propionaldehyde]/M		
0.0016	0.518	0.032
0.0031	1.20	0.038
0.0079	3.39	0.043
0.0146	7.20	0.049
0.049	24.0	0.049
0.076	37.5	0.049
	(Average k_2' 0.044)	
[Formaldehyde]/M		
0.1	2.82	0.002 82
0.2	6.66	0.0033
0.333	10.7	0.003 25
0.666	18.8	0.002 83
1.0	27.5	0.002 75
1.33	35.4	0.002 65
	(Average k_2' 0.0031)	
[Butyraldehyde]/M		
0.005	4.66	0.0926
0.0153	15.8	0.103
	(Average k_2' 0.098)	
[Trichloroacetaldehyde]/M		
0.077	0.323	0.000 424
0.128	0.506	0.000 395
	(Average k_2' 0.000 41)	
[Monochloroacetaldehyde]/M		
0.087	2.52	0.002 89
0.174	5.12	0.002 93
	(Average k_2' 0.002 91)	

[a] $[H^+]$ 0.1M, [PMPA] 5 ± 0.5 × 10^{-4}M, 35 °C, aqueous medium.

Table 3. pH dependence in the PMPA oxidation of formaldehyde [a]

pH	$10^2k_2'_{(obs)}$/ l mol^{-1} s^{-1}	$10^2k_2'_{(calc)}$/ l mol^{-1} s^{-1}
0	1.25	1.25
0.3	0.962	0.994
0.7	0.534	0.618
1.0	0.33	0.379
1.3	0.232	0.214
1.7	0.149	0.093
2.2	0.128	0.057
2.9	0.099	0.0064
3.6	0.467	
4.2	0.654	
4.4	0.802	
4.7	1.93	
5.0	2.699	
5.5	1.021	
6.2	0.944	
7.1	0.201	
7.4	0.157	
8.9	0.317 [b]	
9.0	0.421 [b]	
9.6	2.346	
11.5	25.6 [c]	
11.7	114.0 [c]	

[a] [PMPA] 5 ± 0.5 × 10^{-4}M, [Formaldehyde] 0.21M, aqueous medium. [b] At [Formaldehyde] 0.088M. [c] At [Formaldehyde] 0.0035M.



(S = aldehyde)

Scheme.

H_3PO_5 and $H_2PO_5^-$ are widely different [1,2,4,6,9] in several oxidations by PMPA in which the peroxoacid acts as an electrophile, so that $k_1 \gg k_2$. This reduces equation (2) to (3) or (4). Plots of $1/k_2'_{(obs)}$ *versus* $1/[H^+]$ in the range 0.02—1M-

$$k_2'_{(obs)} = k_1[H^+]/(K_1 + [H^+]) \qquad (3)$$

$$1/k_2'_{(obs)} = 1/k_1 + K_1/k_1[H^+] \qquad (4)$$

$HClO_4$ gave fairly linear plots and permitted us to estimate the values of k_1 and K_1 from the intercept and slopes of the plots. The literature value of K_1 is 0.08 at 25 °C determined by u.v. spectrophotometry [8] and by a kinetic method.[10] The kinetically determined value of K_1 in the present investigation at 35 °C has been found to be 0.34 and is of the right order of magnitude. The values of k_1 for formaldehyde and propionaldehyde are 0.0167 and 0.174 l mol^{-1} s^{-1}, respectively. The fairly good agreement between the calculated and observed values in the pH range 0—2 clearly brings out the dominance of the k_1 step. Using the kinetically determined value of K_1, plots of $k_2'_{(obs)}(K_1 + H^+)$ *versus* $[H^+]$ gave a straight line. For formaldehyde, a small positive intercept gave a value of k_2 (2.77×10^{-4} l mol^{-1} s^{-1}) which is *ca.* 60 times less than the value of k_1 (1.67×10^{-2} l mol^{-1} s^{-1}). A similar plot for propionaldehyde passed through the origin from which the k_2 value which is very small could not be computed. When the literature value of K_1 (0.08) was used, plots of $k_2'_{(obs)}[K_1 + H^+]$ *versus* H^+ resulted in poor straight lines with pronounced deviations at higher acidities.

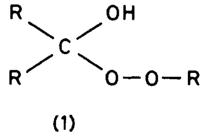
Table 4. pH dependence in the PMPA oxidation of propionaldehyde [a]

pH	$10^2k_2'_{(obs)}$/ l mol^{-1} s^{-1}	$10^2k_2'_{(calc)}$/ l mol^{-1} s^{-1}
0	13.4	12.96
0.3	9.53	10.33
1.0	4.24	3.95
1.3	2.13	2.23
1.6	1.19	1.19
2.3	0.247	0.252
3.4	0.119	
4.3	0.267	
4.6	0.351 [b] (0.353 [c])	
5.1	0.388 [e] (0.378 [d])	
5.3	0.693	
5.6	0.225	
5.7	0.216	
5.9	0.170	
6.2	0.184	
6.9	0.0899	
7.6	0.081	
8.5	0.053	
9.1	0.052	
10.3	0.044	
11.2	0.186	
12.4	1.2	
13.0	15.4	

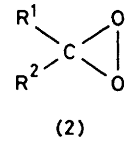
[a] [Propionaldehyde] 8.0 × 10^{-3}M, [PMPA] 5 ± 0.5 × 10^{-4}M, 35 °C, aqueous medium. [b] Phthalate buffer. [c] Acetate buffer. [d] [PMPA] 17.22 × 10^{-4}M. [e] [PMPA] 9.73 × 10^{-4}M.

The most unusual and interesting part of the pH dependence is the maximum in the pH range 3—10. The very low value of k_2 (individual rate constant for $H_2PO_5^-$) suggests that the rate should go on decreasing till pH 10 (where the abundance of HPO_5^{2-} is >95%), until the ionisation of the -O-O-H group begins to be felt. We have observed that in the PMPA oxidation [1] of aniline and *p*-nitroaniline there are rate maxima at pH 4.7 and 1.0 and there is an interesting correspondence with the pK_a of the conjugate acid of aniline (4.60) and *p*-nitroaniline (1.11), respectively. The pH corresponding to the pK_a thus represents a situation where there is the best compromise between the requirements of an unprotonated amine (which will initiate the nucleophilic attack) and the greatest abundance of the more electrophilic oxidant species. The oxidation of aldehydes presents an altogether different situation, where the protolytic equilibria involving the substrate are relatively unimportant. Aliphatic aldehydes are extensively hydrated in aqueous medium and are present as an equilibrium mixture of the carbonyl and hydrate forms. The formation constants are available [7] and there is no dependence on acidity or alkalinity. The fundamental step in peroxide reactions of carbonyl compounds is rapid addition [11] to give a tetrahedral intermediate of type (1). It is thus fair to assume that the >C=O form of the aldehyde is the active species of the substrates.

The maximum in the pH range 3—8 could then be traced to the oxidising species. The only example of which we are aware is the self-decomposition of peroxomonophosphoric acid which has a rate maximum [12] at pH 12.5 nearer to the pK_3 of PMPA. The reaction involves nucleophilic attack by



(1)



(2)

Table 5. Stoicheiometric studies in the oxidation of formaldehyde (HCHO) by PMPA [a]

pH	[HCHO]$_0$/ M	[PMPA]$_0$/ M	Residual [HCHO]/ M	[PMPA]/ [HCHO]
0.3	0.023	0.0075	0.0181	1.53
2.2	0.023	0.008	0.0182	1.66
4.7	0.023	0.009	0.017	1.49
8.3	0.023	0.005	0.018	1.00
12.1	0.024	0.0105	0.0146	1.12

[a] 35 °C, aqueous medium.

PO_5^{3-} on HPO_5^{2-} and the reaction has a second-order dependence on PMPA. The self-decomposition of peroxomonosulphuric acid also has a peak at pH 9.4 corresponding to pK_2.[13] The classical work of Montgomery[14] and Edwards[15,16] has shown that peroxomonosulphate decomposition is ketone catalysed most probably through an intermediate dioxirane (2).

It is of interest to record that the rate maximum is around pH 5—5.3 nearer to the pK_2 of PMPA[7] (5.5) where the distribution of $H_2PO_5^-$ and HPO_5^{2-} is 50% each. It was tempting to see if at this pH there was decomposition of PMPA mediated through the carbonyl group. The self-decomposition of PMPA is negligibly small at this pH. We closely examined the stoicheiometry for this reaction and the results showed that there is indeed significant decomposition in acid medium.

Stoicheiometry and Product Analysis.—Stoicheiometry of the PMPA–formaldehyde reaction was followed at several pH values by two independent methods and the results are given in Table 5. When the ratio of PMPA to aldehyde was *ca.* 3, the residual PMPA was estimated by iodometry at pH 4—5. When the ratio was *ca.* 0.3, formaldehyde was estimated by hypoiodite oxidation. In the pH range 8—12 a clean stoicheiometry of 1 : 1 was observed. Above pH 12, the self-decomposition of PMPA becomes significant, with a second-order dependence on initial [PMPA] and so no attempt was made to determine the stoicheiometry above pH 12. Stoicheiometric measurements by the hypoiodite oxidation in the pH range 0—6 revealed certain unexpected features.

A stoicheiometry higher than one was consistently observed. It would happen only if some PMPA has decomposed. As mentioned earlier, the self-decomposition of PMPA is almost nil till pH 10 and it becomes appreciable at high pH with a maximum at pH 12.5 where the relative abundance of HPO_5^{2-} and PO_5^{3-} is 50% each. The unusual stoicheiometry clearly shows that there is a carbonyl-assisted decomposition of PMPA in the pH range 0—6.

In another experiment propionaldehyde (0.005M) and PMPA (0.012M) were mixed at pH 0.3. Estimation of residual PMPA showed that only 0.003M was left which indicated that more PMPA has reacted than required by a simple stoicheiometry of 1 : 1. The non-stoicheiometric nature of this oxidation shows that the carbonyl compound is also functioning as a catalyst. Thus oxidation of the aldehyde and the decomposition of PMPA may well involve a common intermediate like (2).

In alkaline medium the hydride loss is facile unlike in acidic medium where there is attendant carbonyl-assisted decomposition of the oxidant which is acid independent in the pH range 0—6. Thus, $k_2'_{(obs)}$ is a composite of two rate processes, *i.e.* k_2'(decomposition) and k_2'(oxidation). Admittedly, more work particularly [^{18}O] exchange study is needed to resolve the observed rate constants into k_2'(decomposition) and k_2'(oxidation) to get further insight into the mechanism.

Experimental

All the aldehydes were from B.D.H. An aqueous solution of formaldehyde was obtained by heating paraformaldehyde with H_2SO_4 (1M) and was standardised by oxidation with hypoiodite.[17] Monochloro- and trichloro-acetaldehyde were standardised[18] from the gravimetric yields of 2,4-dinitrophenylhydrazone derivatives.

PMPA used in this study was freshly prepared for each run by the acid hydrolysis of PDP which is a standard procedure[8] and the details of its preparation, estimations, and kinetics have been discussed in our earlier reports.[1-3]

Carbonate-free NaOH was prepared by a standard method[19] and was standardised against succinic acid with phenolphthalein as indicator. Baker analysed 70% perchloric acid was used after proper dilution and standardisation against sodium carbonate. Acetate–acetic acid, potassium hydrogenphthalate–perchloric acid, and potassium dihydrogenphosphate–disodium hydrogenphosphate were used as buffers and the pH of the medium was measured with a Systronics 335 digital pH-meter. The pseudo-first-order rate constants (k_1'/s^{-1}) were calculated from the slope of the log titre *versus* time plots and the second-order rate constants ($k_2'_{(obs)}$/l mol^{-1} s^{-1}) were calculated from equation (5). All kinetic experiments were carried

$$k_2'_{(obs)} = k_1'/[\text{aldehyde}] \qquad (5)$$

out at least in duplicate and the reported rate constants are reproducible to within ±5%.

Due allowance was given to the self decomposition of PMPA while computing oxidation rates in the pH range 12—13. At the highest pH of this study, *i.e.* pH 13 and with an initial PMPA (5 × 10^{-4}M) the self-decomposition was *ca.* 10% in 1 h when the oxidation reaction was essentially complete (more than four half lives).

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