

Reactivities of Mono- & Di-anions of Peroxomonosulphuric Acid towards Benzaldehydes: A Kinetic & Mechanistic Study

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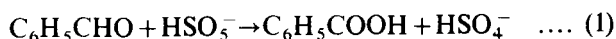
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The rates of reactions of different species of peroxomonosulphate (PMS) with benzaldehydes (BA) have been measured iodometrically in CH₃CN-water mixture in the presence of phosphate buffers. The reaction is overall second order and the rate increases with the increase in pH and is very fast at pH > 8. PMS reacts very slowly with benzaldehydes. The locus of the Hammett plot has a minimum near the point for benzaldehyde for PMS⁻-BA system showing that there is a change in the rate-determining step. A mechanism involving addition/elimination between BA and PMS⁻ near neutral pH has been proposed and thermodynamic parameters for BA-PMS⁻ redox system have been evaluated.

Peroxomonosulphate (PMS) has recently been used as an oxidant in the study of oxidation kinetics of organic compounds¹⁻³. PMS, which is structurally similar to peroxodisulphate (PDS), has been shown to be a better oxidant than PDS in its reaction with halides^{4,5}. The title investigation is an extension of earlier work from our laboratories on the oxidation kinetics of benzaldehydes by a variety of oxidants⁶⁻¹¹.

Benzaldehyde and substituted benzaldehydes, viz. 4-bromo-, 3-nitro-, 4-nitro-, 4-methyl- and 4-methoxy-benzaldehydes (all Fluka products) were used after washing with aq. sodium bicarbonate and distilled/recrystallised. Potassium peroxomonosulphate (Aldrich) a triple salt with the composition 2KHSO₅.KHSO₄.K₂SO₄ was found to be 96% pure when analysed both by cerimetric and iodometric methods. Test for free H₂O₂ in this compound with permanganate was negative. The desired pH was maintained using NaH₂PO₄ and Na₂HPO₄. The course of the reaction was followed iodometrically. Stoichiometric runs revealed that one mol of benzaldehyde consumed one mol of PMS to give the corresponding benzoic acid in accordance with Eq. (1).



Activation energies were determined from Arrhenius plots (for BA-PMS⁻ redox system) in the temperature range 303-323 K. Acrylamide polymerisation test was negative ruling out the involvement of

free radical intermediates during the course of the reaction.

All the experiments were carried out under pseudo-first order conditions, i.e. [BA] ≫ [PMS] (10-fold excess). The variation in pH from 2 to 8 increased the rate constant (Table 1) and the reaction at pH > 8 was almost instantaneous. Hence no experiments could be conducted beyond pH 8. Since peroxomonosulphuric acid has two pK_a values (one in a highly acidic region and the other in the alkaline range, pK_{a2} = 9.4) it is evident that PMS²⁻ is more reactive than PMS⁻ and PMS as such is essentially inert. At pH 5.5 to 6, the reactive species is essentially PMS⁻ and oxidation in this pH range is amenable to kinetic investigation. Under the conditions [PMS⁻] ≪ [BA] the plot of log [PMS⁻] versus time was linear (Fig. 1A) indicating the order in [PMS⁻] as unity. From such plots the pseudo-first order rate constants (k'/s⁻¹) were calculated at varying [BA]. Also the plot of log k' versus log [BA] was linear with a unit slope (Fig. 1B),

Table 1—Effect of pH on k' in PMS-BA System [PMS] = 0.001 mol dm⁻³; [BA] = 0.010 mol dm⁻³; CH₃CN:H₂O = 20:80 (v/v); temp. = 303 K

pH	k' × 10 ³ (min ⁻¹)	pH	k' × 10 ³ (min ⁻¹)
1.89	2.76	4.95	16.7
2.45	4.60	6.30	23.0
3.40	6.90	7.20	26.7
4.30	12.4	8.30	> 140

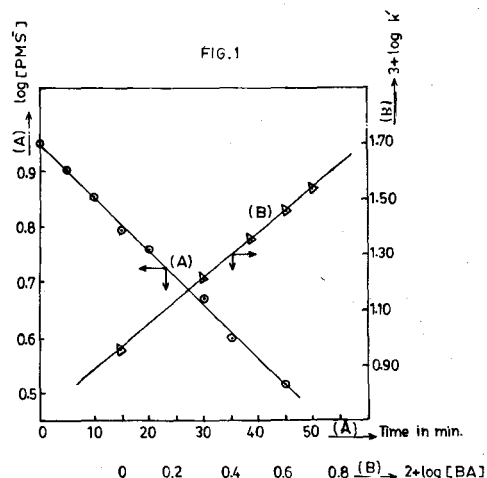


Fig. 1—(A) Plot of log [PMS⁻] versus time ([PMS⁻] = 0.001 mol dm⁻³; [BA] = 0.030 mol dm⁻³; CH₃CN:H₂O = 20:80 (v/v); pH ≈ 6.0; temp. = 303 K) (B) Plot of log [BA] versus log k' (Condition same as in A except [BA] is varied)

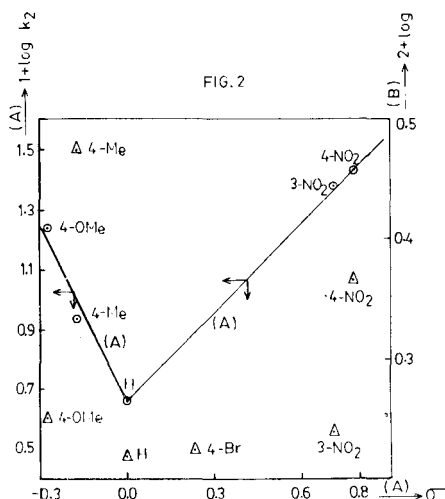
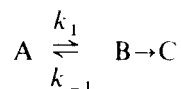


Fig. 2 (A) Plot of $\log k_1$ versus σ for PMS⁻-BA system ([PMS⁻] = 0.001 mol dm⁻³; [BA] = 0.010-0.030 mol dm⁻³; CH₃CN:H₂O = 0.001 mol dm⁻³; [BA] = 0.010-0.030 mol dm⁻³; CH₃CN:H₂O 14 Plot B)

indicating the order in [BA] to be unity. Hence the simplest rate expression is

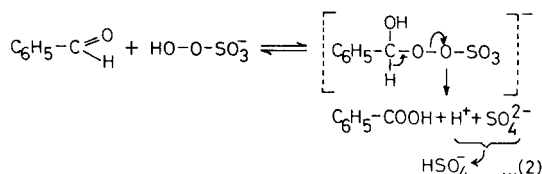
$$\text{Rate} = k_1 [\text{PMS}^-] [\text{BA}]$$

From the data in Table 1 it is clear that the rate constants (k_1) for substituted benzaldehydes with either electron-withdrawing or electron-donating substituents are greater than that of benzaldehyde. Hammett plot, i.e. $\log k_1$ versus σ , consisted of two linear plots (Fig. 2A) converging near the point for benzaldehyde. This type of non-linearity between structure and reactivity was generally attributed to either the change in rate-determining step of a multi-step reaction or when a measured rate constant may actually be a composite quantity depending on the rate and equilibrium constant of several reaction steps. The non-linearity in structure-reactivity is thus for the reactions of the type



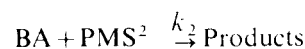
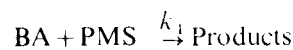
Based on these arguments and for the reason that the reactions were conducted near neutral conditions the probable mechanism for PMS⁻-BA system involving nucleophilic attack of peroxide oxygen on carbonyl carbon, is depicted as shown in Eq. (2)

Such a nucleophilic attack of peroxide oxygen is



very common in the oxidation of sulphur compounds^{3,12} by peroxy anions. It is evident from Eq. (2) that the reversible addition of PMS⁻ to $-\text{C}=\text{O}$ is accelerated by electron-withdrawing substituents on phenyl ring since the nucleophilicity of carbonyl carbon atom increases. This is followed by the elimination of SO₄²⁻ from the adduct, a reaction which is helped by the presence of electron-donating groups in the aromatic nucleus. The balance between these two factors could result in a minimum or maximum in the overall rate. In the present study a minimum rate was observed for benzaldehyde. This type of behaviour is not uncommon in the case of molecule-anion reactions¹³. The activation enthalpy values are as expected for peroxide reactions and are comparable with earlier results¹⁴. The high negative ΔS^\ddagger values clearly indicate extensive hydration of the proton produced during the course of reaction. Oxidations of BA by peroxomonophosphoric acid (PMPA) followed a second order kinetics¹⁴ with a nucleophilic attack of peroxide oxygen on carbonyl carbon of BA. The kinetic and thermodynamic parameters were found to be consistent with an S_N2 mechanism and the rate constants for all substituted benzaldehydes were greater than that of benzaldehyde, though the ρ - σ plot is not v-shaped (Fig. 2B).

PMS can exist in two anionic forms, viz. PMS⁻ and PMS²⁻ depending upon the pH in aqueous solution. Since PMS is inert, both PMS⁻ and PMS²⁻ can be assumed to react with BA.



$$\text{Hence, rate} = k_1 [\text{BA}] [\text{PMS}^-] + k_2 [\text{BA}] [\text{PMS}^{2-}].$$

or

$$\text{rate} = k_1 [\text{BA}] [\text{PMS}^-] + \frac{k_2 k_1 [\text{BA}] [\text{PMS}^-]}{[\text{H}^+]}$$

or

Table 2 Effect of Substituents on k_1 and Thermodynamic Parameters in PMS⁻-BA Reaction

pH \approx 6; CH₃CN:H₂O = 20: 80(v/v); temp. = 303 K

Substituent	k_1 (dm ³ m ⁻¹ s ⁻¹)	E_a	ΔH^\ddagger		ΔS^\ddagger	k_2 (dm ³ m ⁻¹ s ⁻¹)
			(kJ mol ⁻¹)			
H	0.461	5.80	0.60	-273	10.0	
4-NO ₂	2.69	42.5	37.3	-145	45.0	
3-NO ₂	2.40	46.6	41.4	-136	51.7	
4-CH ₃	0.87				75.0	
4-MeO	1.75	39.8	34.6	-165	10.8	

$$-\frac{2.303d \log[\text{PMS}^-]}{dt} = k' = k_1[\text{BA}] + \frac{k_2 k_1 [\text{BA}]}{[\text{H}^+]}$$

A plot of k' versus $1/[\text{H}^+]$ at constant $[\text{BA}]$ was linear from the slope and intercept of which the value of k_2 has been calculated. It is clear from (Table 2) that the k_2 values of all the benzaldehydes are far greater than those of k_1 .

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