

Kinetics of Oxidation of Aromatic Azo Compounds by Peroxymonophosphoric Acid

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The oxidation of aromatic azo compounds by peroxymonophosphoric acid in aqueous HClO_4 -HOAc medium follows total first order kinetics, first order in oxidant and zero order in substrate. Increase in $[\text{H}^+]$ increases the rate, while changes in ionic strength and dielectric constant of the medium have negligible effect on the rate. The plot of $1/k'_0$ versus $1/[\text{H}^+]$ is

linear with a positive intercept and the reaction initiates vinyl polymerisation.

The earlier kinetic investigations on peroxymonophosphoric acid (PMPA) oxidations were confined to the oxidation reactions involving hypophosphite¹, benzaldehyde and substituted benzaldehydes², phenols, acetophenones, amines, *trans*-stilbene, mesitylene, anisole and phenylacetylenes³⁻⁹ as substrates. In all these cases, second order kinetics was reported. In this note, we report the kinetics of oxidation of aromatic azo compounds, viz. methyl orange, *p*-chlorobenzeneazodimethylaniline (*p*-Cl BADMA) and *p*-carboxybenzene-azodimethylaniline (*p*-COOH BADMA) by PMPA.

Potassium peroxydiphosphate was a gift sample from FMC, USA. Doubly distilled conductivity water was used for preparing the solutions.

PMPA was prepared by literature methods¹⁻¹⁰ and standardised iodometrically. For each individual run, a fresh solution of PMPA prepared as above was used. Perchloric acid, acetic acid and sodium nitrate were of A R grade.

Aromatic azo compounds were prepared¹¹ in the laboratory and recrystallised. Solutions (0.1%) of these compounds were prepared in acetic acid and standardised titrimetrically¹². Ionic strength was adjusted with sodium nitrate. The course of the reaction was followed spectrophotometrically by measuring the absorbance of the unreacted azo compound at 510 nm, the absorption maximum of these azo compounds. At this wavelength, other reactants had negligible absorption. Zero order rate constants were calculated for the slopes of plots of absorbance versus time.

The results of stoichiometric runs revealed that one mol of oxidant consumed one mol of the substrate. The products of oxidation were identified as the corresponding azoxy compounds as confirmed by the spot tests¹³.

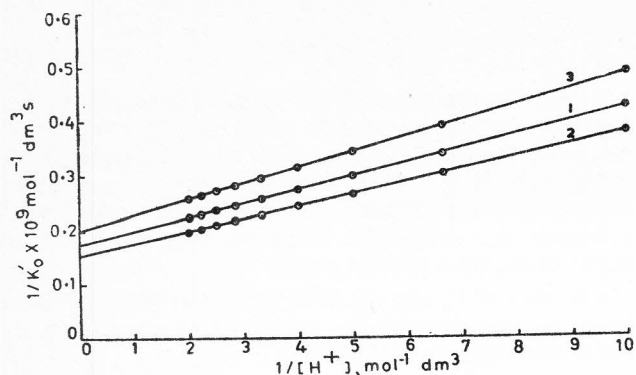
Under the condition $[\text{PMPA}] \gg [\text{azo compound}]$, keeping the concentrations of all the other reactants constant, the rate of the reaction was independent of initial [substrate]. Plots of absorbance versus time in each case were linear. The pseudo zero order rate constants k'_0 calculated from the slopes of these linear plots, were almost equal.

The plot of k'_0 against different initial $[\text{PMPA}]$ was linear passing through the origin, indicating the first order dependence on $[\text{PMPA}]$.

The zero order rate constants k'_0 were determined at different [perchloric acid], keeping the ionic strength constant. Acceleration in the rate with increase in $[\text{H}^+]$ is evident from the rate data in Table 1. The type of dependence of rate on $[\text{H}^+]$, is shown by the linear plot between $1/k'_0$ and $1/[\text{H}^+]$ Fig. 1. From the slope and intercept of the linear plot, the equilibrium constant of protonation of H_2PO_5^- (K) and the specific rate constant (k) for each dye have been evaluated. Changes in ionic strength as

Table 1—Effect of Varying $[\text{H}^+]$ on the Reaction Rate
{ $[\text{PMPA}] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$; HOAc = 5% (v/v); $\mu = 1.0 \text{ mol dm}^{-3}$ [Methyl orange] = $1.69 \times 10^{-5} \text{ mol dm}^{-3}$; [*p*-Cl BADMA] = $2.51 \times 10^{-5} \text{ mol dm}^{-3}$ [*p*-COOH BADMA] = $1.71 \times 10^{-5} \text{ mol dm}^{-3}$ }

$[\text{H}^+]$, mol dm^{-3}	$k'_0 \times 10^3$, mol $\text{dm}^{-3}\text{s}^{-1}$ at		
	30°C	35°C	40°C
<i>Methyl orange</i>			
0.10	2.5	4.2	7.2
0.15	3.0	5.3	9.2
0.20	3.5	6.0	10.5
0.25	3.8	6.7	11.7
0.30	4.0	7.2	12.7
0.35	4.2	7.5	13.3
0.40	4.3	7.8	14.0
0.45	4.5	8.2	14.5
0.50	4.7	8.3	15.0
<i>p</i> -Cl BADMA			
0.10	2.8	5.0	8.7
0.15	3.5	6.3	11.2
0.20	4.0	6.7	13.0
0.25	4.3	8.0	14.3
0.30	4.5	8.5	15.3
0.35	4.8	9.0	16.3
0.40	5.0	9.3	17.0
0.45	5.2	9.7	17.7
0.50	5.25	10.0	18.2
<i>p</i> -COOH BADMA			
0.10	2.0	3.3	5.8
0.15	2.3	4.2	7.3
0.20	2.7	4.8	8.5
0.25	3.0	5.3	9.5
0.30	3.2	5.7	10.2
0.35	3.3	6.0	10.8
0.40	3.5	6.3	11.3
0.45	3.6	6.5	11.7
0.50	3.7	6.7	12.0


 Fig 1—Plots of $1/k'$ versus $1/[H^+]$

{(1) Methyl orange; (2) *p*-Cl BADMA; (3) *p*-COOH BADMA [PMPA] = 8.0×10^{-3} mol dm $^{-3}$; HOAc = 5% (v/v); μ = 1.0 mol dm $^{-3}$; temp. = $30 \pm 0.1^\circ\text{C}$; [Methyl orange] = 1.69×10^{-5} mol dm $^{-3}$; [*p*-Cl BADMA] = 2.51×10^{-5} mol dm $^{-3}$; [*p*-COOH BADMA] = 1.71×10^{-5} mol dm $^{-3}$ }

well as acetic acid concentration of the reaction media did not have any appreciable effect on the rate of the reaction.

The monomers allyl acetate and acrylonitrile, when added initially inhibited the reaction. The reaction mixture was also found to initiate vinyl polymerisation in the absence of atmospheric oxygen.

Peroxyphosphoric acid, a tribasic acid, ionises in accordance with the equilibria (1-3).



From a spectrophotometric study, Battaglia and Edwards¹⁴ calculated the value of K_1 to be 8.9×10^{-2} mol dm $^{-3}$. These workers have reported that PMPA existed as H_3PO_5 and $H_2PO_5^-$ in the pH range 0-2. We believe that these are the important species in the present reaction also.

The reaction is accelerated by increase in $[H^+]$ indicating that H_3PO_5 is the active species of PMPA in the present reaction. Since the reaction obeys first order kinetics in PMPA and zero order kinetics in the substrate, only the former participates in the rate determining step, producing reactive intermediate, which oxidises the substrate in a fast step. The intermediate is different from that obtained through the decomposition of PMPA¹⁵ in alkaline medium. Edwards *et al*¹⁵ have suggested that at low acid concentrations, PMPA decomposes, according to the reaction.

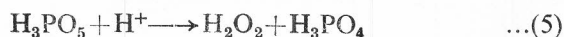


Most probably the aromatic azo compounds are oxidised by the oxygen formed in reaction (4). Hydrogen peroxide formed from the hydrolytic reaction of PMPA (Eq. 5) was ruled out as the

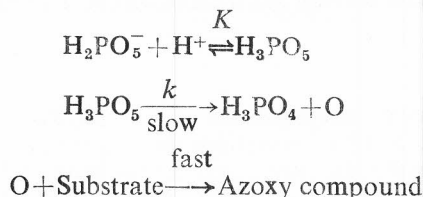
 Table 2—Equilibrium Constant (K), Specific Rate Constants (k) and Activation Parameters

Substrate	K , mol $^{-1}$ dm ^{3} at			ΔH kJ mol $^{-1}$			$k \times 10^7$, s $^{-1}$ at			E_a kJ mol $^{-1}$	$\Delta S^\ddagger$ JK $^{-1}$ mol $^{-1}$
	30°C	35°C	40°C	30°C	35°C	40°C	30°C	35°C	40°C		
Methyl orange	7.1	6.1	5.3	23	7.5	13.8	25.8	99 $\pm$ 2.0	—43.4		
<i>p</i> -Cl BADMA	7.3	6.3	5.4	23	8.3	16.3	31.0	102 $\pm$ 2.0	—31.3		
<i>p</i> -COOH BADMA	7.2	6.2	5.3	23	6.2	11.0	20.7	102 $\pm$ 2.0	—36.7		

reactive intermediate,



because the hydrolysis rate did not reach a limiting value at about 0.5 mol dm $^{-3}$, but increased with further increase in $[H^+]$. Keeping the foregoing discussion in view, scheme 1 is proposed for the oxidation of azo compound by PMPA.



Scheme 1

Scheme 1 leads to the rate law

$$-\frac{d[\text{azo compound}]}{dt} = \frac{kK[H_2PO_5^-][H^+]}{(1 + K[H^+])} \quad \dots(6)$$

In accordance with Eq. (6), the plot of $1/K'$ versus $1/[H^+]$ is linear with positive intercept (Fig. 1). From the intercept and slope, k and K have been calculated at three different temperatures. The value of $K = 6.1$ mol $^{-1}$ dm ^{3} obtained at 35°C and at ionic strength 1 mol dm $^{-3}$ was found to be in reasonable agreement with the values reported by Edwards *et al*¹⁴ (11.23 at 25°C and $\mu = 0.2$ mol dm $^{-3}$) and Gupta *et al*¹ (6.66 mol $^{-1}$ dm ^{3} at 35°C and $\mu = 1$ mol dm $^{-3}$). It may also be noted that nearly the same value of K and ΔH of the protonation of $H_2PO_5^-$ were obtained with each of the azo compounds as substrate. This supports the validity of the rate law and hence the mechanism.

The activation parameters of the rate-determining step are given in Table 2. A low value of $\Delta S^\ddagger$ also lends support to the unimolecular nature of the rate-determining step. For bimolecular rate-determining step $\Delta S^\ddagger$ is generally¹⁻⁹ equal to or more negative than -20 e.u. It was reported by Panigrahi *et al*², that acrylamide did not have any effect on the oxidation of benzaldehyde, presumably due to a concerted transfer of oxygen in the rate-determining step. In the present case, such a concerted transfer of oxygen is not possible because of non-involvement of substrate in the rate-determining step. Consequently, oxygen must be produced in a slow step and reacts with the substrate in a subsequent fast step. This

NOTES

explains the observed inhibitory effect of monomers on rate in the present reaction.

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