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Kinetics and Mechanism of Oxidation of Substituted Benzaldehydes by Peroxydisulphate

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Kinetics of the oxidation of substituted benzaldehydes by peroxydisulphate have been studied. The reaction has a first order dependence on ($S_2O_8^{2-}$) concentration. The rate is independent of the Ag(I) concentration. The rate of oxidation of substrate is dependent on the concentration of substrate. Michaelis Menten type of rate dependence on the substrate has been observed. A tentative mechanism has been proposed based on experimental data.

INTRODUCTION

Kinetics of the oxidation of organic and inorganic compounds by peroxydisulphate has been reviewed by House[1] and by Wilmarth and Haim[2]. So far the oxidation of substituted benzaldehydes has not been studied. The present investigation reports the effect of some substituents in the benzene nucleus on the rate of oxidation of benzaldehyde by peroxydisulphate. Interestingly, in the present investigation no catalysis of Ag(I) ion has been observed.

EXPERIMENTAL

Materials and Method

Substituted *ortho, meta* and *para* benzaldehydes were obtained from K. Light Co., England.

The compounds were distilled and recrystallised. Solutions of substituted benzaldehydes were prepared by dissolving known weight in purified glacial acetic acid and the reactions were carried out in 1.25 M H_2SO_4 and in 70% acetic acid. All other chemicals used were chemically pure. Potassium peroxydisulphate solution was freshly prepared and its concentration checked by iodometry.

Procedure

The rate of oxidation in acetic acid-water mixture (70% AcOH) (v/v) was followed by taking out aliquots of the reaction mixture at different intervals of time, determining the concentrtion of peroxydisulphate left unreacted by the method of Bartlett and Cotman[3]. In general, rates were reproducible to within ±5%.

The reaction of peroxydisulphate proceeded at the same rate in dark and in diffused room light. Hence rates were measured in the diffused light. The values reportes here are corrected for the decomposition of $S_2O_8^{2-}$ under identical conditions. Since the oxidation of various substrates follows the same rate laws both in the presence and absence of oxygen[4-6] no attempt was made to exclude oxygen from the system.

RESULTS AND DISCUSSION

Following conclusions can be drawn from the results of the present study:

1. The reaction is first order with respect to ($S_2O_8^{2-}$). First order rate constants do not show any significant change with change in the initial ($S_2O_8^{2-}$),
2. An increase in (substrate) increased the rate constant,
3. The rate of reaction is independent of Ag(I) concentration (*cf.* Table 1).

TABLE 1
EFFECT OF Ag(I) ON THE OXIDATION OF *p*-NITRO-BENZALDEHYDE AT CONSTANT IONIC STRENGTH

Solvents: 70% acetic acid, 30% water (v/v)
$[S_2O_8^{2-}] = 4 \times 10^{-3}$ M [Substrate] = 4×10^{-2} M
$[H_2SO_4] = 1.25$ M Temperature = 50°C

$[Ag^+] \times 10^4$ M	$k_1 \times 10^4\ sec^{-1}$
5.0	9.99
10.0	9.97
20.0	9.98
30.0	9.96

4. The rate constant increased with increasing acetic acid percentage in the medium (*cf.* Table 2),

TABLE 2
EFFECT OF ACETIC ACID VARIATION ON THE RATE OF OXIDATION OF BENZALDEHYDE

Solvents: 70% acetic acid, 30% water (v/v)
$[S_2O_8^{2-}] = 4 \times 10^{-3}$ M [Substrate] = 4×10^{-2} M
$[H_2SO_4] = 1.25$ M Temperature = 50°C

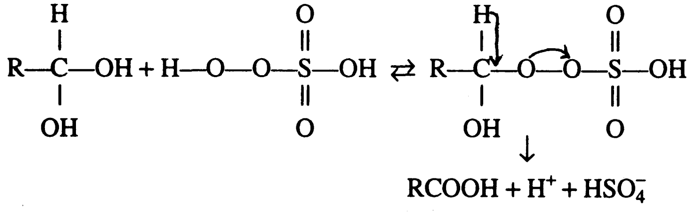
Acetic acid %	$K_1\ 10^4\ sec^{-1}$
40	1.54
50	2.49
60	3.65
70	6.19

5. The rate is approximately proportional to (H^+) ion concentration in the range examined (cf. Table 3).
6. Rate of oxidation in *p*-nitro ≈ *p*-methyl > *m*-nitro > H > *p*-chloro > *o*-nitrobenzaldehyde.

Within the concentration (of the substrate) 8.0×10^{-4} to 2.8×10^{-1} M a plot of $\frac{1}{k_1}$ versus $\frac{1}{(\text{substrate})}$ is linear. This indicates the formation of a complex between substrate and the reactive species and indicates Michaelis and Menten type of rate dependence on the substrate. The rate of these reactions is not affected by the addition of Ag(I) ions (*cf.* Table 1). Further, the oxidation of substituted benzaldehyde is dependent on $[H^+]$ ion concentration. The rate is roughly $\mathrm{p_r}$ oportional to the concentration of $[H^+]$ ion concentration. The rate is roughly proportional to the concentration of $[H^+]$ ions. The oxidation of benzaldehyde by peroxydisulphate in presence of H^+ ion may be schematically represented by one of the following schemes:

Scheme 1

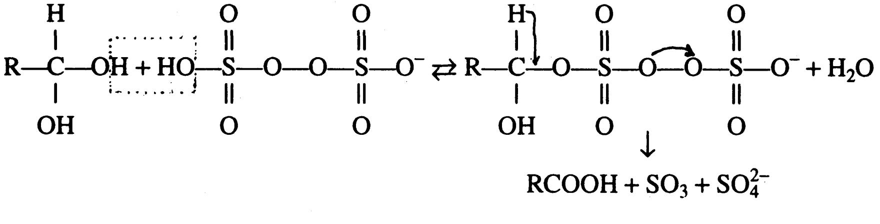
$$S_2O_8^{2-} + H^+ \rightleftarrows HS_2O_8^-$$
$$HS_2O_8^- \rightarrow HSO_4^- + SO_4$$
$$SO_4 + H_2O \rightarrow H_2SO_5$$



$$\mathrm{R{-}\overset{H}{\underset{OH}{C}}{-}OH + H{-}O{-}O{-}\overset{O}{\underset{O}{S}}{-}OH \rightleftarrows R{-}\overset{H}{\underset{OH}{C}}{-}O{-}O{-}\overset{O}{\underset{O}{S}}{-}OH}$$
$$\downarrow$$
$$RCOOH + H^+ + HSO_4^-$$

The rate constant for acid catalysed decomposition of $HS_2O_8^-$ is approximately 5.0×10^{-3} litre mole^{-1} min^{-1} (= 8.2×10^{-5} litre mole^{-1} sec^{-1}).

At the acidities used the rate of decomposition of $HS_2O_8^-$ would be $k_2(H^+) = 7.3 \times 10^{-5}$ sec^{-1}. This is much smaller than the observed rate. The oxidation, therefore, does not proceed through formation of H_2SO_5 (Scheme 1). Alternatively one may think that $HS_2O_8^-$ forms an ester with the hydrated form of the aldehyde and the ester decomposes in the rate determining step.



$$\mathrm{R{-}\overset{H}{\underset{OH}{C}}{-}OH + HO{-}\overset{O}{\underset{O}{S}}{-}O{-}O{-}\overset{O}{\underset{O}{S}}{-}O^- \rightleftarrows R{-}\overset{H}{\underset{OH}{C}}{-}O{-}\overset{O}{\underset{O}{S}}{-}O{-}O{-}\overset{O}{\underset{O}{S}}{-}O^- + H_2O}$$
$$\downarrow$$
$$RCOOH + SO_3 + SO_4^{2-}$$

The evidence for this SO_3 molecule as an intermediate rests on detailed study made by Kolthoff and Miller[8].

TABLE 3
EFFECT OF $HClO_4$ ON THE RATE OF OXIDATION OF BENZALDEHYDE AT CONSTANT IONIC STRENGTH

Solvents: 50% acetic acid, 50% water (v/v)
$[S_2O_8^{2-}] = 4 \times 10^{-3}$ M, [Substrate] $= 4 \times 10^{-2}$M, Temperature = 60°C

$[HClO_4]$M	$K_1 \times 10^4$ sec^{-1}	$K_1 \times 10^4/[H^+]$
0.0	—	—
0.25	0.90	3.60
0.50	1.6	3.20
0.75	2.5	3.33
1.00	3.8	3.80

The effect of the substitutents on the rate has been examined using Hammett equation. A plot of log k/k_0 against σ value is not linear (whether k and k_0 refer to the rate constants of substituted and unsubstituted benzaldehyde respectively (*cf.* Table 4)).

TABLE 4
EFFECT OF SUBSTITUENTS ON THE RATE CONSTANT IN THE OXIDATION OF X.CH_3CHO BY PEROXYDISULPHATE

Solvents: 70% acetic acid, 30% water (v/v)
$[S_2O_8^{2-}] = 4 \times 10^{-3}$ M $[H_2SO_4] = 1.25$ M
Temperature = 50°C [Aldehyde] $= 4 \times 10^{-2}$ M

X	$K \times 10^4$	log k/ko litre mole^{-1} sec^{-1}	σ	σ*
H	4.80	—	—	—
p-Cl	2.88	−0.2218	+0.23	0.144^{++}
p-NO_2	9.98	+0.3179	+0.78	1.27^{+}
p-Me(CH_3)	9.98	+0.3179	−0.17	-0.31^{++}
m-NO_2	5.53	+0.0615	+0.71	—
o-NO_2	2.30	−0.3195	+0.80	—

*Taken from reference 7 pp. 173 (σ); 211 (σ^-) and 204 (σ^+)
*+ refers to σ^-, ++ refers to σ^+

Deviations in Hammett equations are often observed[5, 6, 9] and are sometimes attributed to changes in the relative importance of inductive and resonance interaction mechanism. In some cases, they are sufficiently familiar to warrant the introduction of modified substituent constant σ^+ (in case of resonance interaction of substitutent with the electron deficient site) and σ^- (for reactions involving unshared electron pairs on the carbon atom next to benzene ring). No such correlative improvement could be observed by using σ^+ for *p*-Cl, *p*-CH_3 and σ^- for *p*-NO_2 groups although these modified substituent constants are valid for the oxidation of substituted benzyl alcohols by vanadium[7].

Swain and Langsdorf[10] showed that the reaction constants are not independent of substituent constant and a plot of log k/k_0 versus σ should lead to a curve concave up. According to them, in such a situation, the reaction proceeds by a concerted mechanism where a delicate balance between bond making and breaking steps exists in the transition state. They consider the change in the balance between the processes as a general change in mechanism. Our results also show a curvature, concave up.

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