KINETICS OF OXIDATION OF p-NITROBENZALDEHYDE BY POTASSIUM PERMANGANATE

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ALTHOUGH KMnO$_4$ is one of the most important oxidising agents in laboratory practice, the kinetics of oxidation of Aromatic aldehyde by neutral potassium permanganate have received little study. Tronov[1] determined the rate of reaction between KMnO$_4$ and a number of aldehydes under limited conditions, but he did not attempt to interpret his data in terms of a mechanism. Tompkins[2] found that the oxidation of benzaldehyde with KMnO$_4$ showed a linear increase of rate with increasing hydroxyl ion concentration. Wiberg[3] studied a number of aromatic aldehydes with neutral and alkaline medium and proposed a mechanism. A recent communication on the oxidation of p-nitrobenzaldehyde by KMnO$_4$ in acetic acid medium,[4] prompts us to record our work on the oxidation of p-nitrobenzaldehyde in different buffers in neutral medium and at different temperatures.

All the reagents used were AnalaR grade and p-nitrobenzaldehyde was of Fluka make. The reaction mixture consisted of 38 ml of aldehyde (Ca $2 \cdot 5 \times 10^{-3}$ M), 10 ml of different buffers and 2 ml of KMnO$_4$ (Ca 1×10^{-2} M). The buffer used were phosphate, pH range $5 \cdot 5 - 11 \cdot 0$ and concentrations varied between $\cdot 009$ M to $\cdot 06$ M. Acetate and bicarbonate buffer for pH $6 \cdot 5$ and concentration was between $\cdot 009$ M to $\cdot 06$ M. The pH of the solution was adjusted to the required value by the addition of small amounts of diluted KOH or diluted H$_2$SO$_4$ before the addition of KMnO$_4$. Aliquot quantity of the reaction mixture was pipetted out at successive time intervals into a known excess of acidified KI and liberated iodine was titrated with standard sodium thiosulfate. The over all stoichiometry of the reaction is

$$3RCHO + 2MnO_4^- \rightarrow 2RCO_2^- + RCO_2H$$
$$+ 2MnO_2 + H_2O.$$
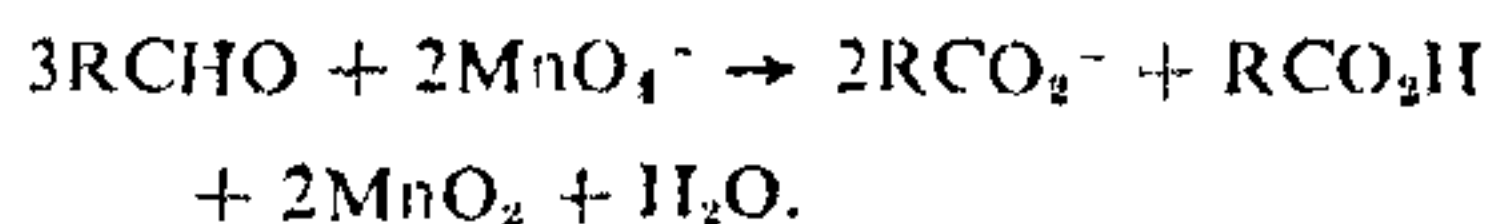
The reaction was found to be first order in permanganate, first order in aldehyde, and the over-all second order constant was calculated by the equation :

$$k = \frac{2 \cdot 303}{t(a-b)} \log \frac{b(a - 3/2\,X)}{a(b - x)}$$

where '*a*' and '*b*' are the initial concentration of aldehyde and permanganate respectively. The experiments were done at different pH using a particular buffer and also at a constant pH using various concentrations of buffers. The temperature range was between 11–40° C.

It was observed that the oxidation of aldehyde is pH dependent as shown in Fig. 1. At lower pH
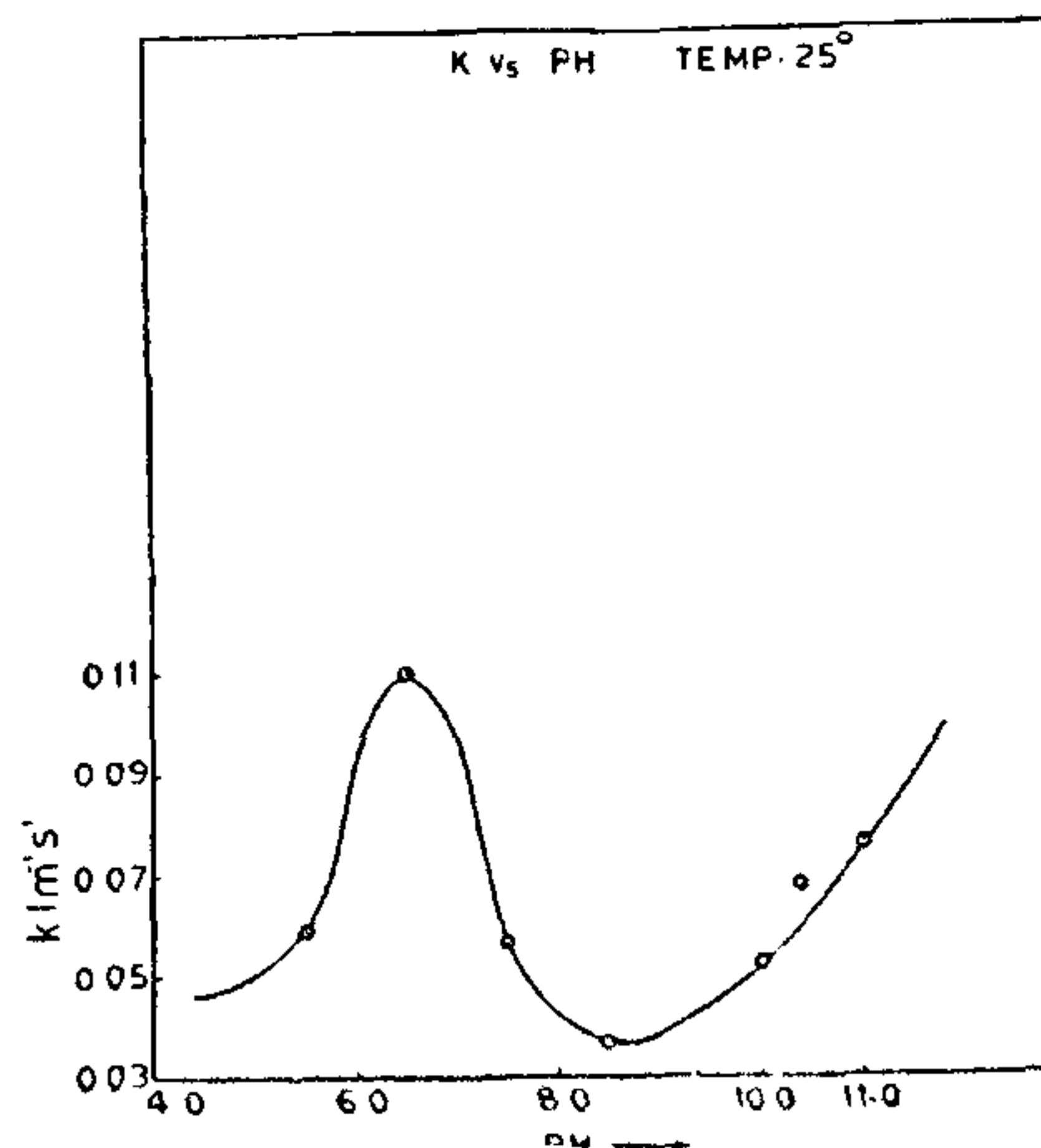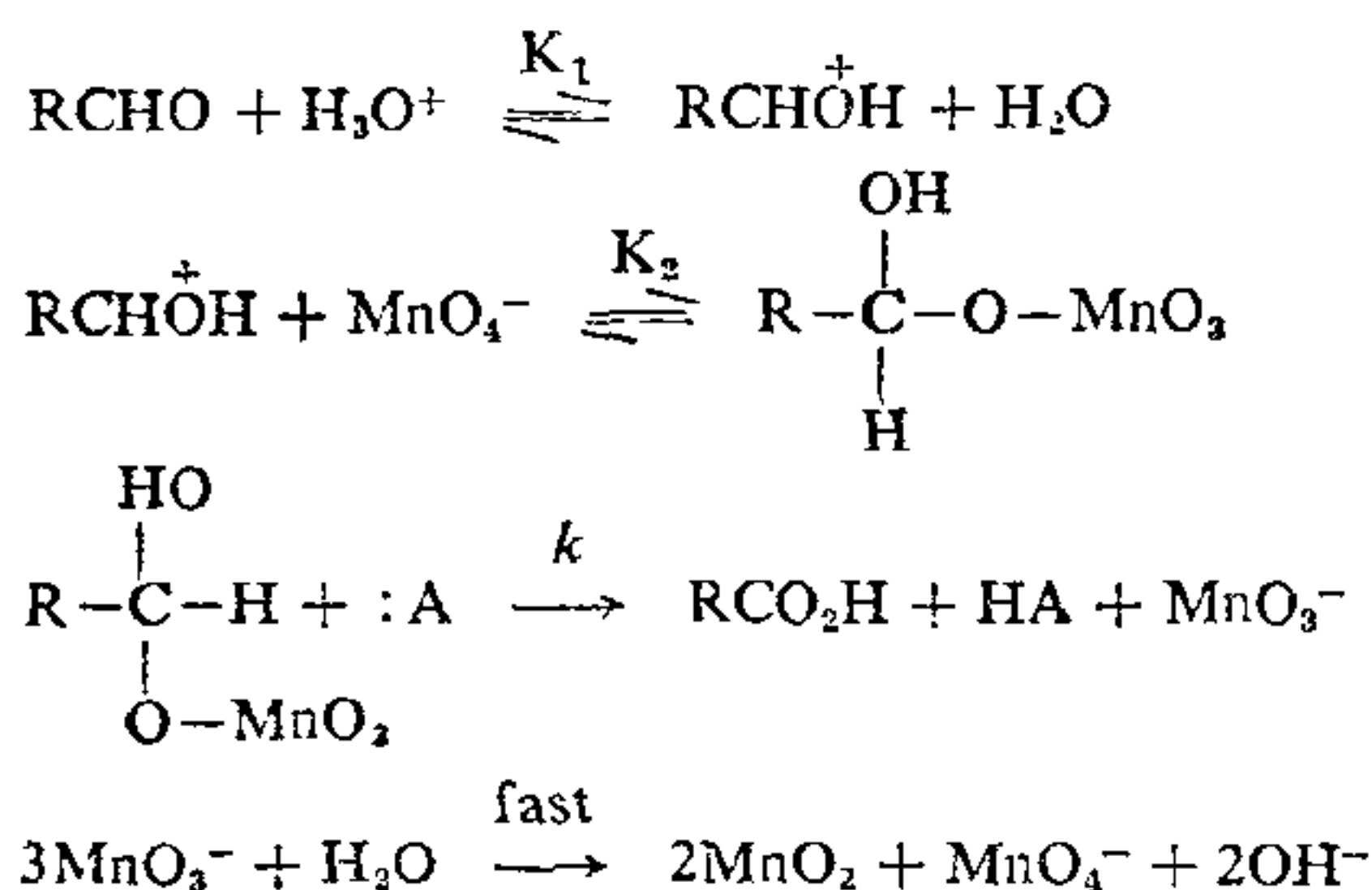

FIG. 1

there is autocatalytic reaction and in the alkaline region (pH 10–12) the rate is directly proportional to the square root of hydroxyl ion concentration. The curve indicates different types of mechanism are operative in the different pH region. The rate constants and other thermodynamic parameters as a function of pH is given in Table I.

TABLE I

Thermodynamic parameters at 25° C in ·02 M NaH$_2$PO$_4$ buffer at different pH $\mu = ·004$

pH	$K_{25°C}$ M^{-1} S$_{ec}^{-1}$	ΔE Kcal mole^1	ΔS Cal/mole
8·5	·03770	9·15	−34·3
7·5	·05757	8·47	−35·4
6·5	·1109	7·32	−38·4
5·5	·05970	7·04	−40·5

Since it was suggested[3] that this reaction may also undergo general acid catalysis, experiments were done at different concentration of buffers and at a constant pH 6·5. Wiberg has proposed the following mechanism for oxidation in the neutral medium :

$$RCHO + H_3O^+ \overset{K_1}{\rightleftharpoons} R\overset{+}{C}H\overset{}{O}H + H_2O$$

$$R\overset{+}{C}HOH + MnO_4^- \overset{K_2}{\rightleftharpoons} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-O-MnO_3$$

$$R-\underset{\underset{O-MnO_2}{|}}{\overset{\overset{HO}{|}}{C}}-H + :A \overset{k}{\longrightarrow} RCO_2H + HA + MnO_3^-$$

$$3MnO_3^- + H_2O \overset{fast}{\longrightarrow} 2MnO_2 + MnO_4^- + 2OH^-$$

If k_1, k_2 and k_3 are catalytic constants for acidic, neutral and general acid catalysis, then it can be shown the over all rate :

$$V = K_1K_2 [RCHO] [MnO_4^-] \{k_1 [H_3O^+]$$
$$+ k_2K_{ic} + k_3K_4 [HA]\}$$

or

$$\frac{V}{[RCHO][MnO_4^-]}$$
$$= k_{II} = K_1K_2\{k_1[H_3O^+] + k_2K_{ir} + K_4k_3 [HA]\}$$

so that at a constant pH and at constant temperature, the plot of second order rate constant *versus* the molar concentration of general acid should be linear and the slope will give $K_1K_2k_3K_4$ where K_i is the ionisation constant of the acid. The slope will be different for different acids. This has been verified for phosphate, acetate and bicarbonate buffers. From the slope it is not possible to calculate k_3, the catalytic constant for general acid catalysis, separately. However, knowing K_i ionisation constant of the general acid, the relative values of k_3 in different buffers can be obtained. The values so calculated are :

$$k_{NaH_2PO_4} : k_{KHCO_3} : k_{NaAc} :: 1 : 0·32 : 0·002$$

indicating that the phosphate catalysis the reaction much faster than bicarbonate or acetate.

1. Tronov, B. V., *J. Russ. Phy. Chem.*, 1927, 59, 1155.
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4. Manjrekar, S. K., Rajagopalan, S. and Soman, S. V., *Ind. J. Chem.*, 1973, 11, 564.

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