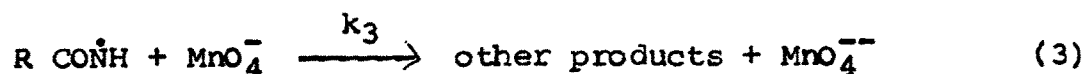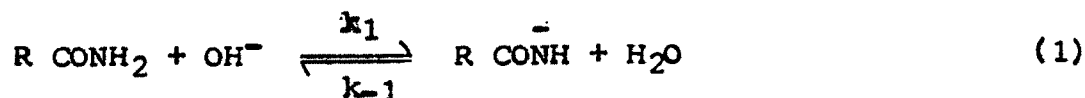CHAPTER VI : PROBABLE REACTION MECHANISM AND RATE LAW

Keeping the experimental facts in view, the probable reaction mechanism is shown in Scheme-I.

$$R\ CONH_2 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\ \overset{-}{CONH} + H_2O \qquad (1)$$

$$R\ \overset{-}{CONH} + MnO_4^- \xrightarrow{k_2} R\ \overset{\cdot}{CONH} + MnO_4^{--} \qquad (2)$$

$$R\ \overset{\cdot}{CONH} + MnO_4^- \xrightarrow{k_3} \text{other products} + MnO_4^{--} \qquad (3)$$

where R is C_5H_4N group.

Scheme-I

The formation of the anion of the amide. Step-I in scheme-I is supported by the observation of Stewart and co-workers[1] who have studied the kinetics of permanganate oxidation of alcohols in alkaline medium and suggested that the alkoxide ion formed by the ionisation of alcohols in one of the reacting species.

Now considering the steady state conditions for these steps the rate law in terms of the decreasing concentration of permanganate would be

$$-\frac{d\left[MnO_4^-\right]}{dt} = 2\ k_2 \left[R\overset{-}{CONH}\right]\left[MnO_4^-\right] \qquad (1)$$

and $R\ \overset{-}{CONH}$ comes out to be

$$\left[R\ \overset{-}{CONH}\right] = \frac{k_1\left[RCONH_2\right]\left[OH^-\right]}{k_{-1}\left[H_2O\right] + k_2\left[MnO_4^-\right]} \qquad (2)$$

Since H_2O is present approximately in constant quantity so it might be taken in k_{-1}. Thus, equation (2) reduces to

$$\left[\overline{RCONH}\right] = \frac{k_1 \left[RCONH_2\right]\left[OH^-\right]}{k_{-1} + k_2 \left[MnO_4^-\right]} \tag{3}$$

Now from equation (1) and (3) the final rate law results.

$$V_i = \frac{- d \left[MnO_4^-\right]}{dt} = \frac{2\, k_1\, k_2 \left[RCONH_2\right]\left[OH^-\right]\left[MnO_4^-\right]}{k_{-1} + k_2 \left[MnO_4^-\right]} \tag{4}$$

where V_i is the rate of disproportionation of $KMnO_4$.

The rate law (4) clearly accounts the observed experimental data in first order kinetics with respect to acetamide and hydroxide ion.

Now, on the basis of experimental results the following inequality would manifest.

$k_2 \left[MnO_4^-\right] \gg k_{-1}$, and the rate law (4) finally reduces to (5).

$$V_i = \frac{- d \left[MnO_4^-\right]}{dt} = 2\, k_1 \left[RCONH_2\right]\left[OH^-\right]$$

The rate law (5) clearly accounts zero order kinetics with respect to permanganate and first order with respect to amide and hydroxide ion.
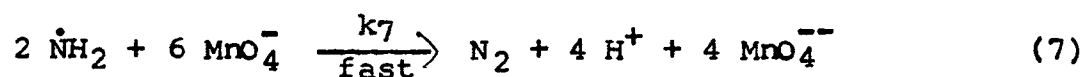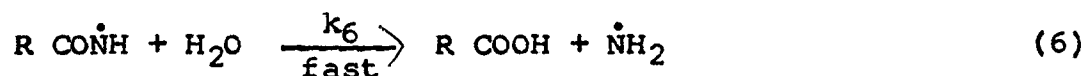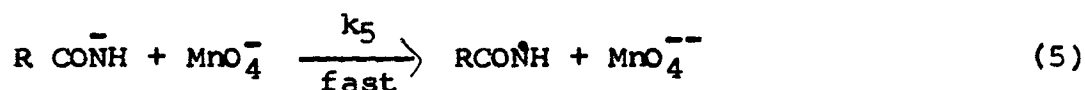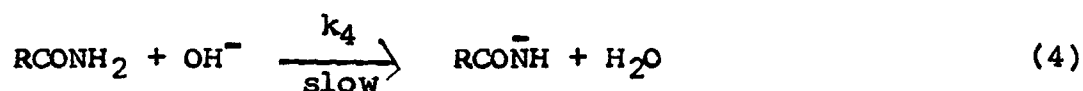
Now, the rate law (5) might be varified with the help of the plot between V_i against the concentration of hydroxide ion. The straight line obtained which clearly accounts the validity of the derived rate law on the basis of the proposed probable reaction path.

Similarly, the rate law (5) again be varified on plotting V_1 against the concentration of amide. In this case the straight line also been obtained.

A close examination of the values of the k_1 obtained from two different methods (i.e. from hydroxide ion variation and amide variation) clearly suggests that the validity of the derived final rate law (5) and hence confirms the proposed reaction mechanism.

Scheme-II

When the experimental results are revisualized, it is possible to propose an other reaction path. Considering other factors of the reaction the scheme II can be proposed in the following lines.

$$RCONH_2 + OH^- \xrightarrow[slow]{k_4} RC\overset{-}{O}NH + H_2O \qquad (4)$$

$$R\ C\overset{-}{O}NH + MnO_4^- \xrightarrow[fast]{k_5} RC\overset{\cdot}{O}NH + MnO_4^{--} \qquad (5)$$

$$R\ CO\overset{\cdot}{N}H + H_2O \xrightarrow[fast]{k_6} R\ COOH + \overset{\cdot}{N}H_2 \qquad (6)$$

$$2\ \overset{\cdot}{N}H_2 + 6\ MnO_4^- \xrightarrow[fast]{k_7} N_2 + 4\ H^+ + 4\ MnO_4^{--} \qquad (7)$$

In above scheme-II, the step (4) is supposed to be slow and the rate determining step. In presence of alkaline $KMnO_4$ the amide anion might be oxidised fast resulting amide free radical. The free radical would again react with one mole of H_2O producing acid and amine radical. In step (7) amine radical will again oxidise fast producing nitrogen. On the

basis of the above scheme-II the rate law might be derived from steady state conditions and it comes out to be

$$- \frac{d\left[MnO_4^-\right]}{dt} = k_4 \left[RCONH_2\right]\left[OH^-\right] \tag{6}$$

where k_4 is the second order velocity constant.

A close examination of the rate law (5) and (6) indicates that both the rate laws are similar although they had been derived from two different reaction paths.

In scheme-II, the step (5) has been supposed to be fast, but it is quite unusual because a reaction between two similar charged ion can not be fast. Thus, on the basis of Debye-Huckel limiting law the step (5) can not be supposed fast. Hence we might safely conclude at this stage that the scheme-II will not be operating.

From the experimental data, it has been observed that the order of reaction with respect to $KMnO_4$ is zero and according to the law of mass action the consumption of $KMnO_4$ must occur in fast step. We have proposed a step (2) in scheme I to be slow. This point is quite valid from the point of view of salt effect. Such type of results in the oxidation of sugars by alkaline ferricyanide[2] and copper(II)[3] had been explained by Singh and co-workers and they have also taken ferricyanide and copper in slow step. Thus, we are quite justified in proposing the scheme-I for the oxidation of amides by alkaline $KMnO_4$.

It has already been suggested by Michaelis[4] that all oxidations of organic molecular proceed in two successive univalent steps via intermediate free radicals. The final oxidation product, acid has been confirmed with the help of chromatographic technique. Thus the reaction mechanism proposed and the derived rate law clearly accounts the experimental data.

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