Free radical intervention in the oxidation of nicotinamide by alkaline permanganate – A kinetic study

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The reaction proceeds in two different stages. A mechanism is proposed and the constants involved in the mechanism are evaluated. The activation parameters for the slow step were calculated and are discussed.
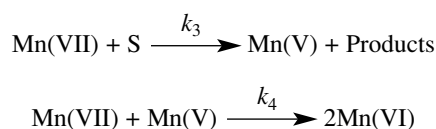
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During oxidation by permanganate, it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which the multivalent oxidant oxidises a substrate depends not only on the substrate but also on the medium[9] used for the study. In strongly alkaline medium, the stable reduction product[10,11] of permanganate is manganate ion, MnO_4^{2-}. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn(VI) (Scheme 1) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by a rapid oxidation of the hypomanganate ion[12] (Scheme 2)

$$Mn(VII) + S \xrightarrow{k_1} Mn(VI) + S^*$$

$$Mn(VII) + S^* \xrightarrow{k_2} Mn(VI) + Products$$
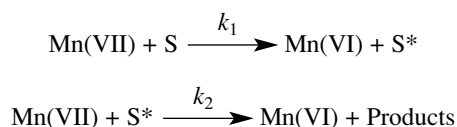
Where, S = substrate: $k_2 \gg k_1$

Scheme 1

$$Mn(VII) + S \xrightarrow{k_3} Mn(V) + Products$$

$$Mn(VII) + Mn(V) \xrightarrow{k_4} 2Mn(VI)$$

Where, S = substrate: $k_4 \gg k_3$

Scheme 2

The kinetics of oxidation of nicotinamide by permanganate in aqueous alkaline medium at a constant ionic strength of 2.0 mol/dm^3 was studied spectrophotometrically. The reaction is of first order in [KMnO4] and of zero order in [nicotinamide] and less than unit order in [alkali] under the experimental conditions in both the stages of reaction. The reaction rate increases with increase in ionic strength and with decreasing solvent polarity of the medium. Initial addition of reaction products did not affect the rate significantly.

Permanganate ion, MnO_4^-, is a powerful oxidant in an aqueous alkaline medium. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the prevailing experimental conditions at pH > 12, the reduction product of Mn(VII) is stable and further reduction of Mn(VI) might be stopped.[10,11] The diode array rapid scan spectrophotometric (DARSS) studies have

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shown that at pH > 12, the product of Mn(VII) is Mn(VI) and no further reduction was observed as reported[21] earlier. The reaction between nicotinamide and permanganate in alkaline medium has a stoichiometry of 1:2, with less than unit order dependence on alkali, zero order dependence on nicotinamide concentrations and a first order dependence on permanganate concentration in both the stages. No effect of the products was observed. It is interesting to note here that zero order dependence with respect to nicotinamide concentration is observed in both the stages which is a rare case. The results indicate that first the alkali combines with permanganate to give an alkali-permanganate species $[MnO_4.OH]^{2-}$ in a prior equilibrium step.[22] This species decomposes in a slow step to give manganate ion and hydroxyl radical.[23] The active radical, (OH$^•$) interacts with nicotinamide to give a nicotinic acid and amino free radical ($\overset{•}{N}H_2$) in a fast step. Such a type of free radical ($\overset{•}{N}H_2$) formation is in accordance with earlier work.[24] The formed nicotinic acid reacts with another molecule of the active species of permanganate and free radical ($\overset{•}{N}H_2$) in a further fast step to give the products. Since the reaction orders are the same in both stages, a single mechanism is proposed as given in Scheme 3.
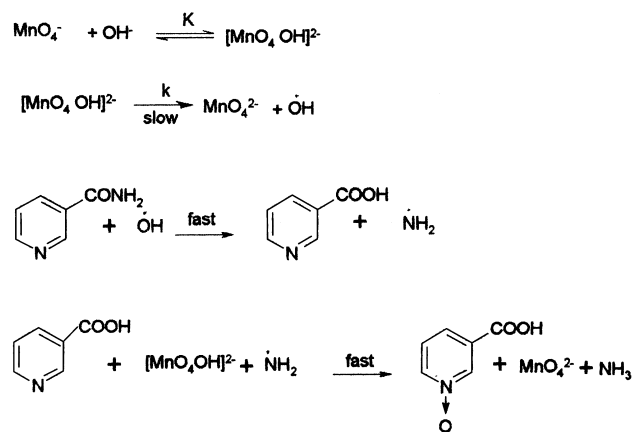
Scheme 3

Since Scheme 3 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in a sequence of one electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work[25] on the alkaline permanganate oxidation of various organic substrates. Scheme 3 leads to the rate law (2).

$$\text{Rate} = -\frac{d[MnO_4]}{dt} = \frac{k\,K[MnO_4]_T[OH^-]_T}{(1 + K[OH])(1 + K[MnO_4^-])} \quad (2)$$

Terms such as $(1 + K[MnO_4^-])$ in the denominator of equation (2) approximate to unity in view of low concentration of MnO_4^- used. Therefore equation (2) becomes equation (3)

$$\frac{Rate}{[MnO_4^-]} = k_{obs} = \frac{kK[OH^-]}{1 + K[OH^-]} \qquad (3)$$

Thus, equation (3) can be rearranged to the following form which is used for the verification of the rate law:

$$\frac{1}{k_{obs}} = \frac{1}{kK[OH^-]} + \frac{1}{k} \qquad (4)$$

According to equation (4), the plots of $1/k_{obs}$ versus $1/[OH^-]$ should be linear which is verified in Fig. 5. The slope and intercept of such plots lead to the values of K and k at 25°C as 3.18 ± 0.11 dm^3/mol and $1.12 \pm 0.05 \times 10^{-2}$ s^{-1}, respectively, for the first stage. Using these values, the rate constants under different experimental conditions were calculated. Experimental and calculated values of k_{obs} agree reasonably well, supporting the assumptions of Scheme 3. The value of K and k are in good agreement with earlier work.[26] Similarly the value of K and k were calculated from such plots at 25°C for second stage of the reaction as, 10.2 ± 0.3, dm^3/mol and $1.8 \pm 0.05 \times 10^{-3}$ s^{-1}, respectively. Using these values, rate constants under different conditions were calculated for the second stage and are in good agreement with observed values (Table 1).

The effect of increasing ionic strength on the rate qualitatively explains the reaction between the two negatively charged ions as shown in Scheme 3. The effect of solvent on the reaction kinetics has been described in detail in the literature.[27] Increasing the content of t-butanol in the reaction medium leads to increase in the rate of reaction, which is contrary to the expected slower reaction between like ions in the media of lower relative permittivity. Perhaps this effect is opposed substantially by an increased formation of active reaction species to a greater extent in low relative permittivity media, thus leading to the observed net increase in reaction rate.[28]

The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favourable for electron transfer processes. The favourable enthalpy was due to release of energy on solution changes in the transition state. The values of $\Delta S^{\#}$, within the range of radical reactions, have been ascribed[29] to the nature of electron pairing and electron unpairing processes and to the loss of a degree of freedom, formerly available to the reactions on the formation of rigid transition state.

Reasons for two stages: Details regarding the occurrence of two stages can be furnished as follows. It is suggested that these stages are probably[30] due to creation of optimum concentration of intermediates or due to consecutive reaction. Here it may be expected that the second stage portion of the plot may be interpreted as the rate of oxidation of the resulting nicotinic acid to N-oxide of nicotinic acid as the final product. This is also evidenced by comparing the rate constants of second stage with that of the direct oxidation of nicotinic acid by permanganate[31] which are nearly same under the experimental conditions.

Techniques used: Spectrophotometry, and IR.

References: 29

Tables 2

Figure 1: Spectral changes in the oxidation of nicotinamide by permanganate

Figure 2: Plot of log $[MnO_4^-]$ versus time,

Figure 3: Plot of log k_f versus $I^{1/2}$ and log k_S versus $I^{1/2}$

Figure 4: Plot of log k_f versus 1/D and log k_s versus 1/D

Figure 5: Plots of $1/k_f$ versus $1/[OH^-]$ and $1/k_s$ versus $1/[OH^-]$ (Conditions as in Table 1)

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