E2-48 Kinetics and mechanism of oxidation of ethylacetate by $KMnO_4$ in acidic medium

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Metal ions/complexes play a dominant role in synthetic organic chemistry as they have the potential to oxidise a wide variety of organic compounds. Although considerable work has been done on the oxidation of organic compounds by $KMnO_4$, very little attention has been paid to the kinetics of oxidation of esters. In our continuing effort to examine products and rates of oxidation of organic compounds by metal ions/complexes, the reaction between ethylacetate and $KMnO_4$ in acidic medium is reported.

Kinetic studies were carried out under pseudo-order conditions by reacting $KMnO_4$ with excess ethylacetate (EtAc) under acidic conditions in aqueous acetonitrile. The progress of the reaction was monitored colorimetrically by measuring the decrease in absorbance of $KMnO_4$ at 520 nm with time at different EtAc concentrations at constant pH and vice versa.

Analysis of kinetic data revealed that the reaction exhibits a rate law:

$rate = k[KMnO_4][EtAc][H^+]^2$,
where overall rate constant, $k=2.58 \times 10^{-4} mol^{-3}l^3s^{-1}$ at 303K.

The final product of the reaction has been identified as acetic acid. The toichiometry of the reaction was established as $KMnO_4$: EtAc = 2:1.

A mechanism involving a rapid equilibrium to form a powerful oxidant $H_2MnO_4^+$ followed by slow attack of $H_2MnO_4^+$ on the alcohol moiety of the ester with the transfer of a hydride ion to the oxidant to form acetic acid and acetaldehyde has been proposed. The latter is subsequently oxidised to acid by a similar mechanism.

Proposed mechanism:

$$MnO_4^- + 2H^+ \underset{\text{fast}}{\rightleftharpoons} K \quad H_2MnO_4^+$$

$$CH_3COOC_2H_5 + H_2MnO_4^+ \xrightarrow[\text{slow}]{k} CH_3COOCH^+CH_3 + H_3MnO_4$$

$$CH_3COOC^+HCH_3 \xrightarrow[\text{fast}]{H_2O} CH_3COOH(OH)CH_3 + H^+$$

$$CH_3COOCH(OH)CH_3 \xrightarrow{\text{fast}} CH_3COOH + CH_3CHO$$

$$CH_3CHO + H_2MnO_4^+ + H_2O \longrightarrow H_3COOH + H_3COOH + H_3MnO_4 + H^+$$

$$2H_3MnO_4 \xrightarrow{\text{disproportionation}} H_2MnO_4 + MnO_2 + 2H_2O$$