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Kinetics of Manganese(III) Oxidation of Anisic Acids and Alcohols

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Manganese(III) oxidation of anisic acids and glycols has been studied in the presence of perchloric acid. The reaction exhibits a total second order kinetics, first order in each reactant. The effect of temperature on the oxidation has been investigated in the temperature range 293–323 K and the thermodynamic parameters have been calculated. The formation of the product in each case is accounted by a suitable mechanism.

INTRODUCTION

Manganese(III) can be used as oxidant for a variety of organic and inorganic substrates[1–4]. It has been found that the oxidation of organic substrates results in the formation of radical ion intermediates. The radical cation then loses a proton in a slow rate-determining step to form a radical, which undergoes further rapid oxidation of product. Kinetics of oxidation of various aromatic compounds by Mn(III) has been studied by Dewar and others[5, 6]. The investigations support the mechanism involving electron transfer. The oxidation of aromatic hydrocarbons[7] by manganese(III) proceeds by two mechanisms, *viz.*, a free radical mechanism and an electron transfer mechanism. Santappa and coworkers[8] carried out extensive studies on the oxidation of unsaturated acids by manganese(III) and suggested a mechanism involving a complex intermediate between the substrate and manganese(III). To prove the mechanistic aspects of manganese(III) oxidation of organic substrates, kinetics of oxidation of anisic acids and glycols by manganese(III) has been studied.

RESULTS AND DISCUSSION

Oxidation of Anisic Acids: Kinetics of oxidation of three methoxybenzoic acids namely *p*-anisic acid (PAA), *o*-anisic acid (OAA) and *m*-anisic acid (MAA) has been carried out. When equal concentrations of the oxidant and reductant are used, kinetic data fits into the second order rate equation and the rate constant value increases with increase of initial concentration of the reactants. Thus the total order of the reaction is two. In order to establish the order with respect to substrate, kinetic measurements are made under pseudo first order conditions. The plot of log K_1 values against log (PAA) gives a straight line with a slope of unity. The order with respect to oxidant determined by differential method is also found to be unity. The effect of temperature on the rates of oxidation of three anisic acids by Mn(III) in dry acetic acid has been investigated in the temperature range 293–323 K. These reactions exhibit Arrhenius dependence and the activation energies are calculated from Arrhenius plots. The thermodyanmic parameters are calculated using Eyring's equation. The energy of activation (E_a), the enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and log A values are given (Table-1) for the anisic acids. The order of activity is PAA > OAA > MAA. The entropy of activation values are negative indicating that the transition state is more solvated[•] than the reactants. The products formed are found to be dimethoxybiphenyl derivatives which is confirmed by TLC and PMR spectral data. The PMR spectra of the products have two signals, one a multiplet around 5.5–7.0 δ and the other at 3.8 δ. The PMR spectral data showed that the products formed are biphenyl derivatives. The reaction mixture gives a polymer when treated with acrylonitrile and it also gives a white precipitate with mercuric chloride. The tests indicate the formation of a radical intermediate. Consistent with the above results, the following mechanism could be proposed for the oxidation of *p*-anisic acid and manganese(III).

Mechanism

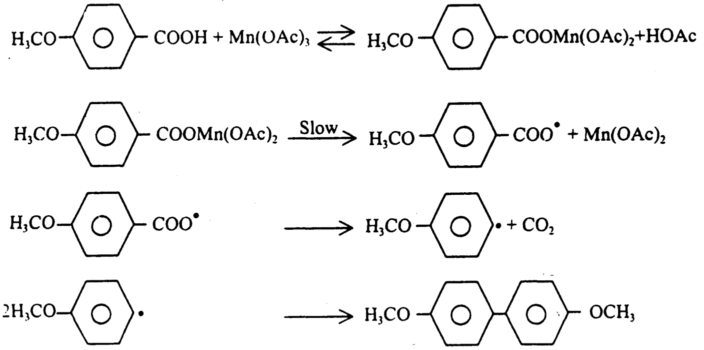


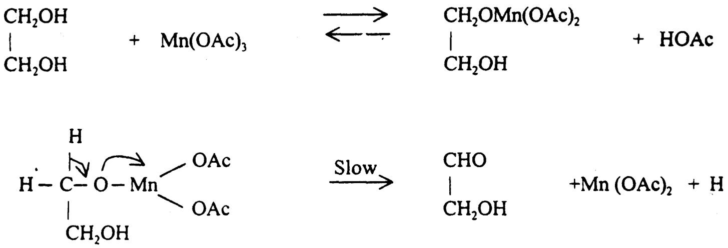
TABLE-1

THE OXIDATION OF ANISIC ACIDS AND GLYCOLS BY MANGANESE(III) ACETATE

Reductant	E_a, kJ mol^{-1}	$\Delta H^{\#}$, kJ mol^{-1}	$\Delta S^{\#}$, J K^{-1} mol^{-1}	log A
PAA	36.78	34.22	–172.85	4.6405
OAA	56.19	53.64	–116.15	7.6018
MAA	85.01	82.45	–18.96	12.6778
EG	19.96	17.40	–216.91	2.338
PG	25.22	22.67	–231.13	1.598
MEG	46.76	44.20	–154.89	5.578

Oxidation of Alcohols: Kinetic studies have been carried out on three alcohols, ethylene glycol (EG), propylene glycol (PG) and monomethyl ether of ethylene glycol (MEG). The overall order of the reaction was found to be two. The order of the reaction with respect to substrate was found under pseudo first order conditions. The log K_1 values are plotted against log [substrate] which gives a straight line with a slope of unity. The order with respect to oxidant, determined by differential method, is also found to be unity. The effect of temperature on the reaction of Mn(III) oxidation of alcohols is studied under pseudo first order conditions and values of Arrhenius activation energy and thermodynamic parameters are calculated (Table-1). The E_a values indicate that the order of reactivity is EG > PG < MEG. In EG, Mn(III) can attack either of the two hydroxyl groups and hence the reaction is faster. When one of the hydroxyl groups is methylated, the oxidant can react with only one hydroxyl group and hence monomethyl ether of EG is less reactive than EG. The slow reactivity of propylene glycol than ethylene glycol can be explained as follows. The product analysis of these reactions indicates that in all cases the primary alcoholic group is oxidised to an aldehyde. The products formed are confirmed by TLC and PMR spectra. Hence Mn(III) appears to be a selective oxidant for primary alcohol. In the absence of a primary alcoholic group it may oxidise the secondary alcohol at a slower rate. Since only one primary alcoholic group is present in PG, oxidation of PG by Mn(III) is slower than that of EG. Considering the above factors the following mechanism could be proposed for the Mn(III) oxidation of ethylene glycol.

Mechanism



EXPERIMENTAL

Manganese(III) acetate (Fluka) was used as such and the assay of the sample was estimated to be 99%. Dry acetic acid was obtained according to the reported procedure[9, 10]. Organic substrates were purified by recrystallisation or fractional distillation, following the reported procedures[11].

Solutions of substrates were prepared in dry acetic acid and those of the oxidant were prepared in dry acetic acid in the presence of 0.2 N perchloric acid. The flask containing manganese(III) acetate was covered with black paper as it is photosensitive.

The standard solutions were thermostated for nearly half-an-hour at a specific temperature and mixed. Definite volume of aliquot of the reaction mixture was pipetted at various time intervals to follow the course of the reaction. The concentration of the unreacted oxidant was estimated by iodometry[11]. The reactions were carried out under pseudo first order conditions. The rate constant were obtained from the plot of $1/(a-x)$ or $\log(a-x)$ *vs.* time. The velocity measurements for all the substrates were done over the temperature range 293–323 K and the activation energies were obtained by least square analysis.

The reaction mixture was kept aside for 4 h at 303 K with excess of oxidant. The mixture was neutralized with sodium carbonate and the organic product was separated by ether and then analysed by TLC and spectral techniques. In order to establish the formation of free radical intermediate, polymerisation test and mercuric chloride test were made. The stoichiometry was established in all the reactions for varying concentrations of the oxidant and reductant and it was found to be 1 : 1 corresponding to oxidant : reductant.

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