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Kinetics and Mechanism of Propane-1,3-diol Oxidation by Mn(VII) in Aqueous Medium

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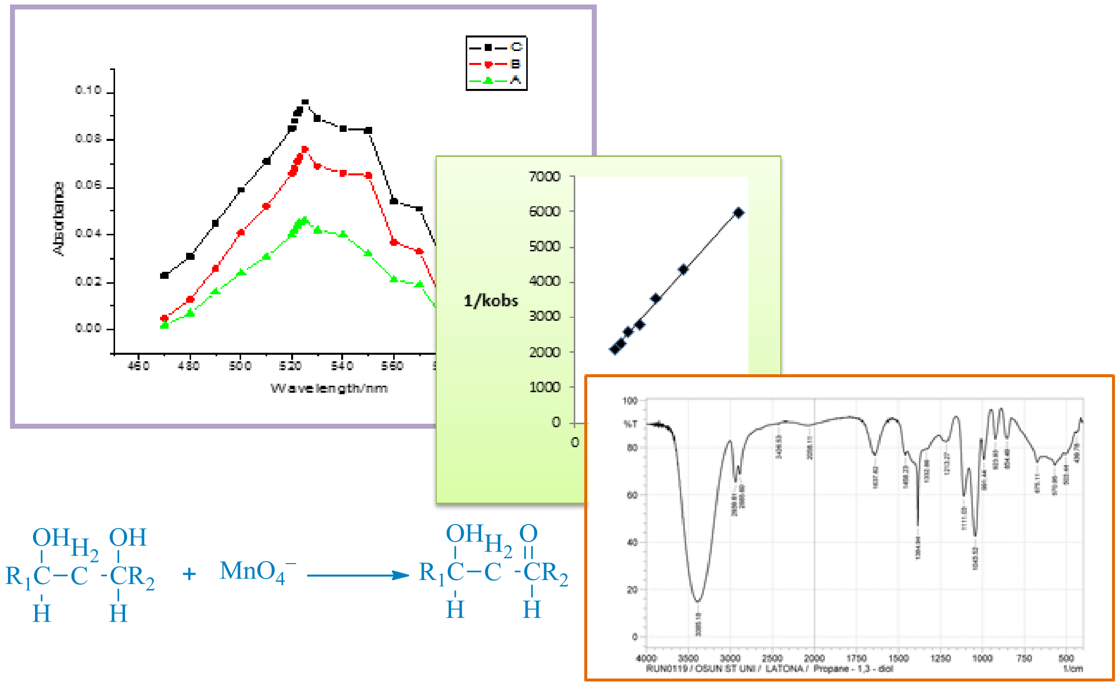
ABSTRACT

The oxidation of propane-1, 3-diol by potassium permanganate in aqueous solution was investigated at λ_{max} 525 nm. The rate of the reaction was found to increase with increase in [$KMnO_4$] and [Propane-1, 3-diol]. The reaction showed first order dependence each in [$KMnO_4$] and [Propane-1, 3-diol] and independent in the ionic strength of the solution. The values of $\Delta H^{\#}$(kJ mol^{-1}), $\Delta S^{\#}$ (kJK^{-1}mol^{-1}) and $\Delta G^{\#}$(kJ mol^{-1}) were 24.98, -0.22 and 90.50 respectively. Negative activation of entropy revealed an ordered transition state for the reaction. Spectroscopic studies and FTIR analysis revealed the product of the reaction to be 3-hydroxy-propanone.

GRAPHICAL ABSTRACT



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Introduction

Potassium permanganate discovered by Margueritte in 1846 has now been widely used for redox reactions involving a variety of chemical reactions. It is a versatile strong oxidizing agent in both acidic and alkaline media which has been employed for the oxidation of various organic compounds like alcohols [1-3], aldehydes and ketones [4-6], amines [7], glyoxal and glyoxalic acid [8]. There are few reports in the literature on the oxidation of Diols. Howeve r, oxidants like tetrabutylammonium tribro mide(TBATB)[9], cerium(IV)[10,11], benzyl trimethylammonium tribromide [12], 12-tungstocobaltate(III) anion[13], trialkylam monium fluorochromates(VI) [14], tripropylammonium fluorochromate[15], barium manganate[16] have been employed for the oxidation of diols. Oxidation of diols by Mn (VII) has not been reported in the literature. Therefore, this research is aimed at investigating the kinetics and mechanism of the oxidation of propane-1, 3-diol by a strong oxidant like $KMnO_4$.

Experimental

Materials and methodology

Potassium permanganate(AR), Propane-1,3-diol(BDH), Potassium nitrate(AR), Ferrous ammonium sulphate(AR) and sulphuric acid(BDH) were used without further purification by preparing their stock solutions in doubly distilled water. Potassium permanganate was standardized using Ferrous ammonium sulphate in acidic medium. The kinetic study was done using 1800 UV-Shimadzu Spectrophotometer with a thermostated cell compartment and interfaced with a computer. Freshly prepared solutions were used in all the kinetic studies. The ionic strength of the solution was kept constant with potassium nitrate.

Kinetic Study

The oxidation reaction was studied under pseudo-first order kinetics by keeping concentrations of propane-1, 3-diol in excess of potassium permanganate concentrations at 298K. Appropriate quantities of the reaction mixtures of propane-1, 3-diol and potassium nitrate were measured into the cuvette. Consequently, the reaction was initiated by adding requisite volume of $KMnO_4$ solution. All stock solutions were kept in a water bath for 30 minutes before the kinetic runs. Progress of the reaction was followed by monitoring decrease in absorbance of $KMnO_4$ as a function of time at λ_{max} 525 nm. The pseudo-first order rate constant (k_{obs}) were obtained from a plot of In A versus time.

Stoichiometry

The stoichiometry was accomplished by

spectroscopic titration at 525nm. The absorbance at infinite time of reaction mixtures containing different initial concentrations of propane-1, 3-diol within the range 2.66×10^{-3}- 1.07×10^{-2} M at fixed [$KMnO_4$] and ionic strength at 3.97×10^{-5} and 6.67×10^{-3} M respectively were obtained. Consequently, the stoichiometry of the reaction was determined from the plot of Absorbance at infinite time versus concentration of propane-1, 3-diol. The stoichiometry was found to be one mole of $KMnO_4$ per one mole propane-1, 3-diol.

Product analysis

A solution of 2 drops of the product in 2ml of 95% ethanol was added to 3ml of 2, 4-dinitrophenylhydrazine reagent. Formation of a precipitate confirms the presence of carbonyl compound [17].

Induced polymerization of acrylamide

The oxidation of the vicinal diols by $KMnO_4$, in nitrogen atmosphere did not induce polymerization of acrylamide.

Effect of potassium permanganate concentration

The effect of $KMnO_4$ was studied with the view to ascertaining the order of reaction with respect to [$KMnO_4$]. This was done by varying [$KMnO_4$] within the range $9.37 \times 10^{-6}M \leq [KMnO4] \leq 6.67 \times 10^{-5}M$ at fixed [Propane-1, 3-diol] and ionic strength at 4.00×10^{-3}M and 6.67×10^{-3}M respectively.

Effect of propane-1, 3-diol concentration

The effect of [Propane-1, 3-diol] on the oxidation reaction was carried out with the view to obtaining the order of reaction with respect to the diol and also to ascertain the second order rate constant of the reaction. More so, to confirm whether the oxidation reaction followed Michaelis-Menten kinetics. The effect of propane-1,3-diol concentration on the reaction was studied by varying [Propane-1,3-diol] within the range $1.34 \times 10^{-3}M \leq [\text{Propane-1,3-diol}] \leq 1.07 \times 10^{-2}M$ and fixing [$KMnO_4$] and ionic strength at 3.97×10^{-5}M and 6.67×10^{-3}M respectively.

Effect of ionic strength

The effect of ionic strength was determined in order to determine the ions present at the rate determining step. This was carried out by varying the ionic strength of the reaction solution within the range $1.33 \times 10^{-3}M \leq \mu \leq 1.33 \times 10^{-2}M$ and keeping concentrations of $KMnO_4$ and propane-1,3-diol constant at 3.97×10^{-5}M and 4.00×10^{-3} M respectively at 298 K.

Effect of temperature

Activation parameters were determined from temperature dependent study by fixing [$KMnO_4$], [Propane-1,3-diol] and ionic strength, μ at 3.97×10^{-5} M, 4.00×10^{-3} M and 6.67×10^{-3} M respectively and varying temperature of the reaction mixtures within

298K ≤T≤ 318K. Activation parameters were obtained from the below equations [18].

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{RT} + \ln\left(\frac{k^{/}}{h}\right) + \left(\frac{\Delta S^{\ddagger}}{R}\right)$$

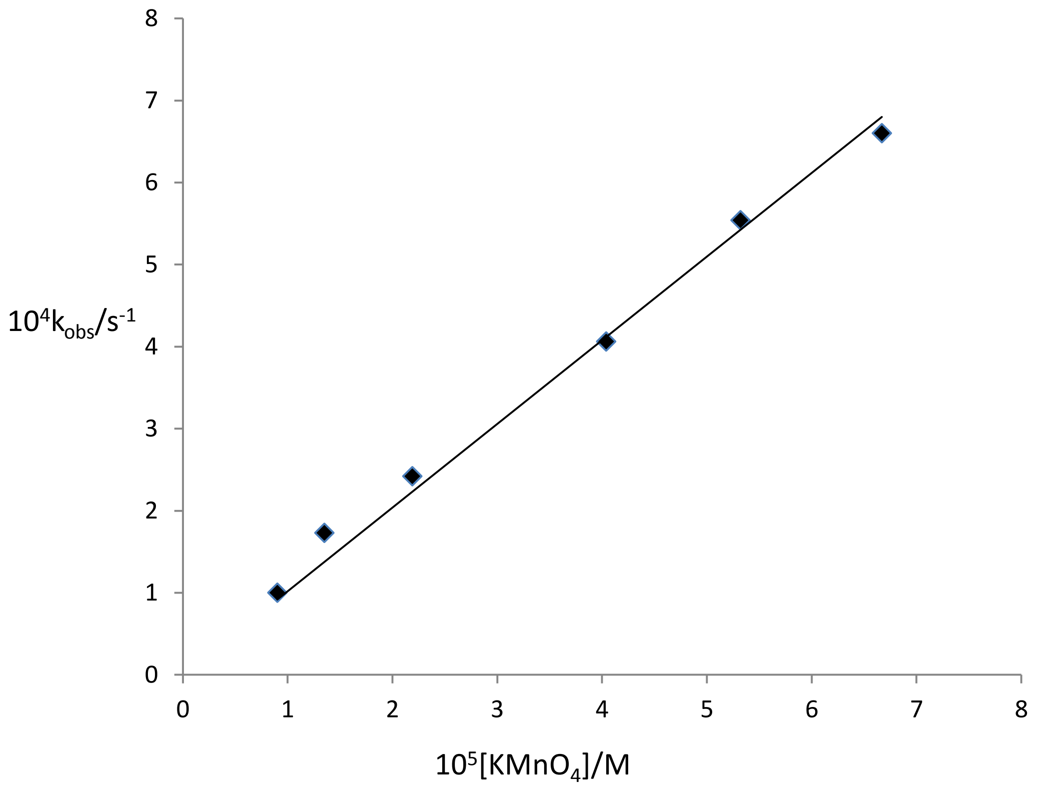
$$\ln\left(\frac{k^{/}}{h}\right) = 23.76$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

Where k is the observed rate constant, T is Temperature in Kelvin, $\Delta H^{\#}$ is Enthalpy of activation $\Delta S^{\#}$ is Entropy of activation, $\Delta G^{\#}$ is Free Gibb's energy of activation, R is the Molar gas constant $k^{/}$ is Boltzmann's constant and h is the Planck's constant

Reaction orders

Pseudo-first order rate constant (k_{obs}) increased with increase in the concentration of $KMnO_4$ (Figure 1). The order is unity with respect to [$KMnO_4$]. Increase in pseudo-first- order rate constant (k_{obs}) with increase in diol concentration was observed (Table 1) and the slope of in k_{obs} versus In [Propane-1, 3-diol] gave 1, indicating a first order dependence with respect to diol concentration.



Scheme 1. Effect of [$KMnO_4$]

Table 1. Effect of [Diol]

10^3[Diol]/M	$10^4k_{obs}/s^{-1}$
	Propane-1,3-diol
2.66	1.67
4.00	2.30
5.34	2.82
6.67	3.56
8.00	3.86
9.34	4.42
10.70	4.83

Second order rate constant obtained from the slope of the plot of k_{obs} versus [Propane-1, 3-diol] was $4.87 \times 10^{-2} M^{-1}s^{-1}$. Variation of ionic strength of the reaction mixture using KNO_3 did not affect the rate of reaction, implying the presence of a neutral molecule at the rate determining step. There was a considerable increase in the pseudo-first order rate constant (k_{obs}) with increase in temperature (Figure 2) and activation parameters in Table 2 were obtained from Arrhenius and Erying's equations.

Spectral Studies

The spectral of $KMnO_4$ and $KMnO_4$ + Propane-1,3-diol at three different concentrations of diol indicated an increase in the absorbance of $KMnO_4$ as the concentration of diol increases (Figure 4). However, the absorbance of the reaction mixture decreased with time. This revealed the formation of an intermediate pre-equilibrium complex which led to product formation [4].

Rate law

Michaelis-Menten plot of $1/k_{obs}$ versus 1/[Diol] gave a straight line graph with an intercept, indicating the presence of an intermediate complex (Figure 3). The kinetic study showed first order dependence on each of [$KMnO_4$] and [Diols].

$$\text{diol + oxidant} \underset{k_{-1}}{\rightleftharpoons} \text{complex}$$

$$\text{complex} \xrightarrow{k_2(\text{slow})} \text{products}$$

Applying steady state approximation:

$$\text{Rate} = k[\text{diol}][\text{oxidant}]$$

where, $k = \frac{k_2 k_1}{k_{-1} + k_2}$

Mechanism of reaction

The use of quinolinium dichromate for the oxidation of non-vicinal diols yielded α-hyroxy carbonyl compounds with a mechanistic pathway involving the intermediate formation of a chromate ester, which undergoes decomposition to yield the product [18]. FTIR spectrum analysis of product showed no observable oxidation of the second hydroxyl group in the diol.

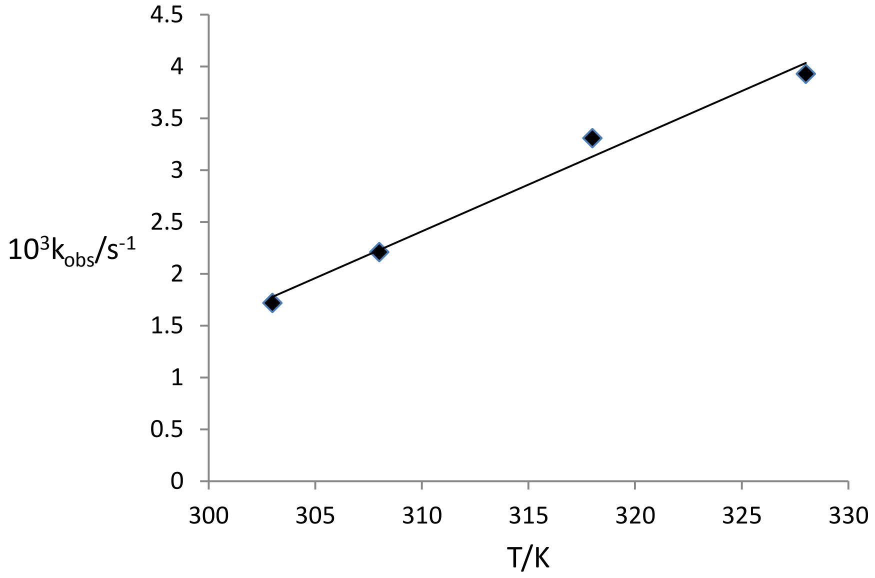


Figure 2. Effect of temperature

Table 2. Activation parameters

Diol	Ea(kJ mol^{-1})	Δ$H^{\#}$(kJ mol^{-1})	Δ$S^{\#}$ (kJK^{-1}mol^{-1})	Δ$G^{\#}$(kJ mol^{-1})
Propane-1,3-diol	27.53	24.94	-0.22	90.50

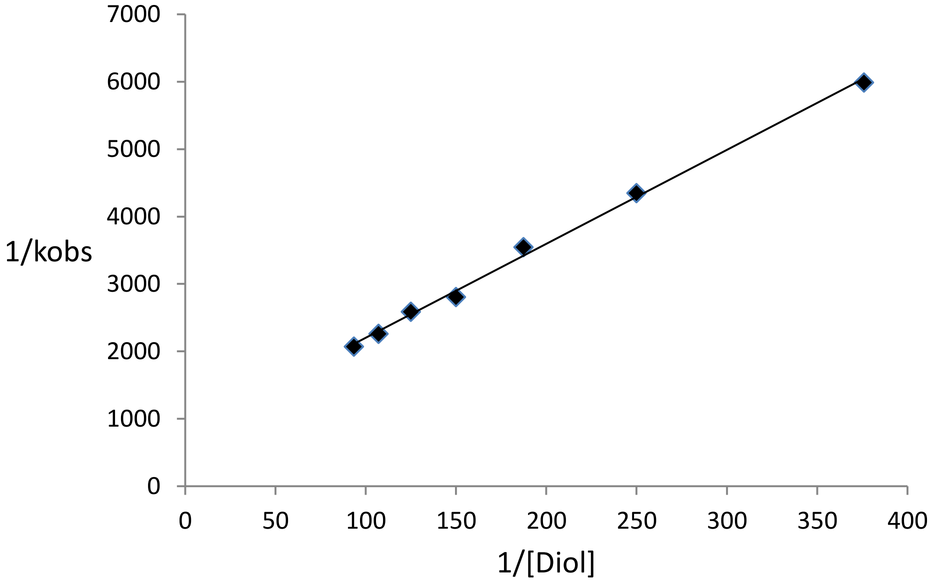


Figure 3. Michaelis-menten plot

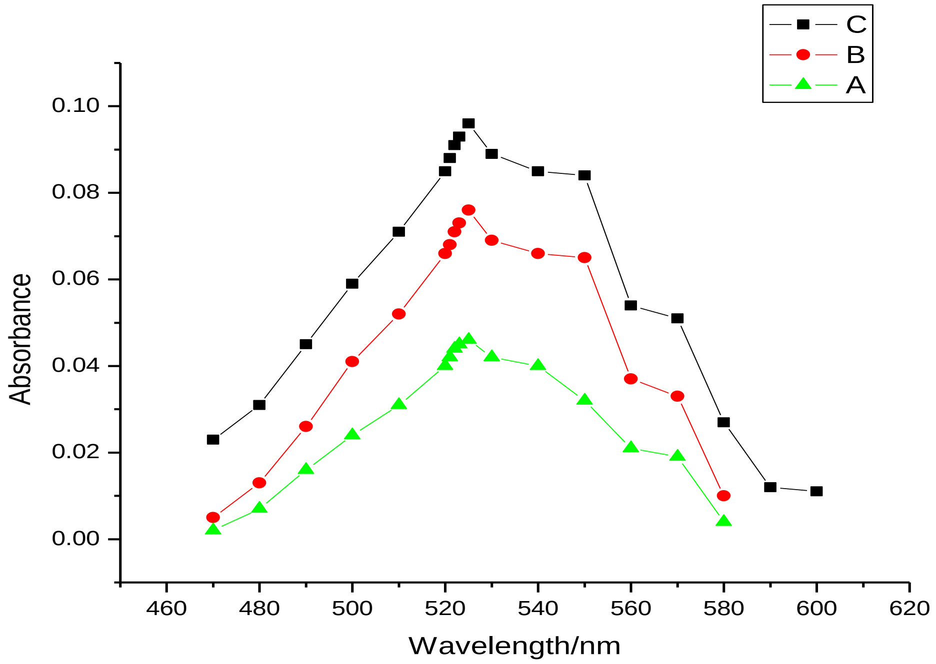


Figure 4. UV-VIS spectra of [A] 3.97×10^{-5} mol dm^{-3} $KMnO_4$ + 1.34×10^{-3} mol dm^{-3}, Diol + 6.67×10^{-3} KNO_3 mol dm^{-3}, [B] 3.97×10^{-5} mol dm^{-3} $KMnO_4$ + 5.34×10^{-3} mol dm^{-3}, Diol + 6.67×10^{-3} KNO_3 mol dm^{-3}, [C] 3.97×10^{-5} mol dm^{-3} $KMnO_4$ + 8.00×10^{-3} mol dm^{-3} Diol + 6.67×10^{-3} KNO_3 mol dm^{-3}

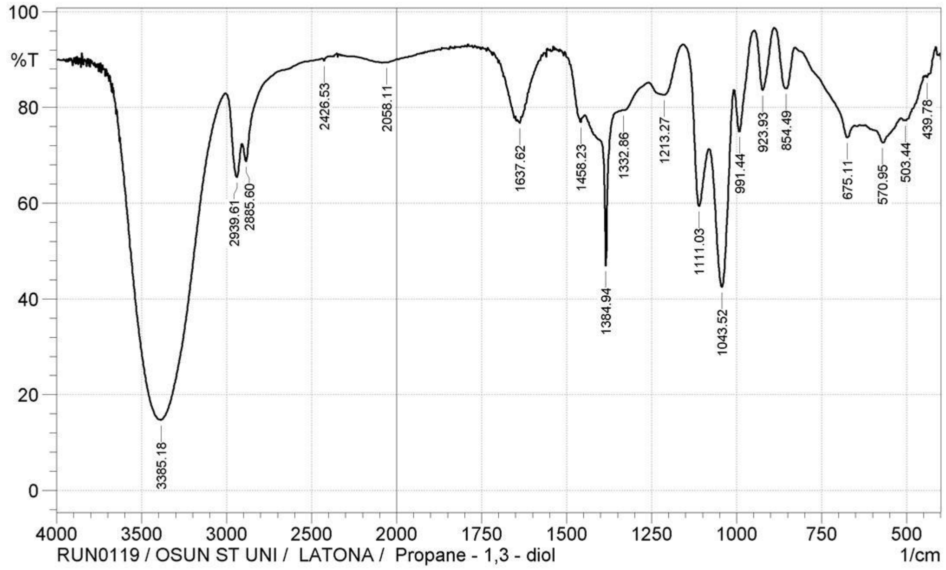
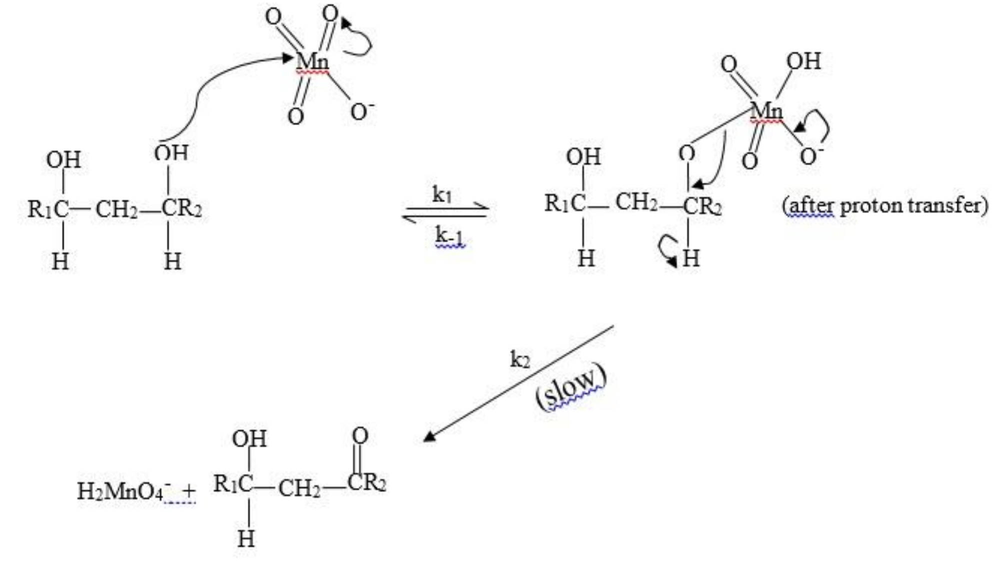


Figure 5. FTIR-spectrum of the product

The FTIR spectrum showed O-H broad peak at 3200-3500 cm^{-1} and C=O stretching at 1690-1760 cm^{-1} of ketones. A hydrogen abstraction mechanism of one-electron oxidation leading to the formation of free radicals is ruled out due to lack of polymerization with acrylamide [19]. The overall mechanism is proposed to involve the formation of a manganate ester in a fast pre-equilibrium step and then a decomposition of the ester to product as shown in Scheme 1. When an anion reacts with a neutral molecule to form an intermediate complex as in this case, the charge is dispersed over large area in the product. Hence the charge density is reduced and the complex formation is enhanced by decrease in the water content of the solvent mixture [12]. Negative value of $\Delta S^{\#}$ indicates an associative mechanism and a rigid transition complex [20].



Scheme 1. Oxidation reaction

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