The plot $\phi_V - 1.868 \sqrt{c}$ for sodium valerate passes through a minimum at a concentration of 0·5-0·6 moles litre[-1]. Desnoyers and Arel[6] have explained the occurrence of minimum in ϕ_V for alkyl ammonium salts in water on the basis of hydrophobic hydration (before minimum) and micellization (after minimum). Seen in this light the cmc value for sodium valerate is 0·5 mole litre[-1] which is in excellent agreement with the value reported from osmotic coefficient study of this salt[20].

From the viscosity behaviour of this salt, it can be seen that viscosity B coefficient is very high. Subtracting the B coefficient value of sodium ion (0·08)[12] from the total, one can obtain the value for valerate ion (0·72). When this value is compared with the value for acetate ion (0·25)[12], it can be said that valerate ion is a strong structure former than acetate ion, which is expected since the hydrophobic residue in valerate ion is more strong than acetate ion. The comparison of ionic B coefficient with molecular B coefficients shows that ions have very high values (acetic acid = 0·12, valeric acid = 0·26). The behaviour of acetate ion has been explained by Gurney[12] on the basis that acetate ion is stabilized by forming stronger hydrogen bonds than the acid molecule. The same explanation can be applied to explain the behaviour of valerate ion. Thus strong ion-solvent interactions should lead to higher B coefficient for anion than that of the parent molecule which is indeed the case.

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Kinetics & Mechanism of Oxidation of Isobutyric & Diglycolic Acids by Manganic Ion†

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The kinetics of oxidation of isobutyric acid (IBA) and diglycolic acid (DGA) have been carried out in the temperature range 15-45° in aqueous sulphuric acid medium. The reaction is overall second order-first order with respect to each reactant. The absence of spectral changes of manganese (III) acetate on adding diglycolic acid and isobutyric acid confirms the outer-sphere interaction of the substrate and the oxidant. The energy of activation and other thermodynamic parameters have been evaluated and discussed. A mechanism involving free radical intermediate is proposed.

THE kinetics of oxidation of alcohols, carboxylic acids, ketones and aldehydes by manganese(III) have been widely studied. Manganese(III) pyrophosphate[1], manganese(III) sulphate[2], manganese(III) perchlorate[3,4] and manganese(III) acetate[5,6] have been used as oxidants. Manganese(III) acetate has been mostly used in non-aqueous medium. The kinetics of reaction of manganese(III) perchlorate with isobutyric acid has been studied by Wells et al.[3]. But no detailed kinetic study has so far been made for the oxidation of isobutyric acid (IBA) and diglycolic acid (DGA) by manganese(III) acetate in aqueous medium.

Manganese(III) acetate was prepared as per the literature procedure[5]. Isobutyric acid was purified by distillation under reduced pressure. Diglycolic acid (Fluka), sulphuric acid (Basynth, AR, sp. gr. 1·8), sodium bisulphate (E. Merck) and manganese-(II) acetate (LR, BDH) were used as such.

The reaction system consisted of manganese(III) acetate $(4 \times 10^{-3} M)$, substrate (0·04 to 0·4M), [H+] (2·5M) with a total volume of 50 ml and at an ionic strength of 2·6M. All the components except manganese(III) acetate were placed in a reaction flask which was thermostated. At definite intervals, after adding manganese(III) acetate, 2 ml aliquots were taken and run into 2% potassium iodide solution to arrest the reaction. The resulting solution of iodine was titrated against standard sodium thiosulphate solution.

At constant [substrate], [H₂SO₄] (2·5M), μ (2·6M) and temperature, a first order dependence with respect to [Mn³⁺] was observed. The plot of $-R_{Mn}$ versus [Mn³⁺] was linear with zero intercept (Fig. 1). At constant [Mn³⁺] (0·004M), [H₂SO₄] (2·5M), μ (2·6M) and temperature variation of excess of [substrate] gave increasing rates with increasing [substrate]₀. From the linear plots of log [Mn³⁺] versus time, the pseudo unimolecular
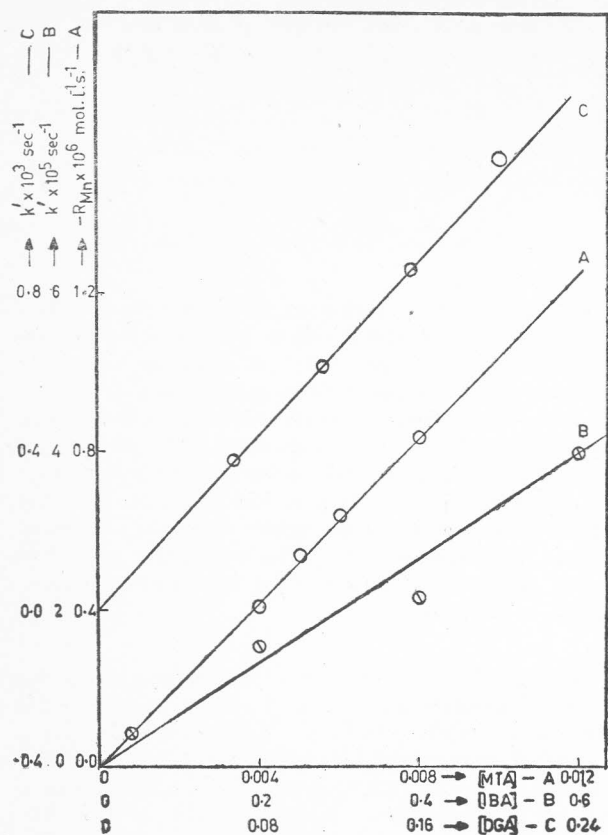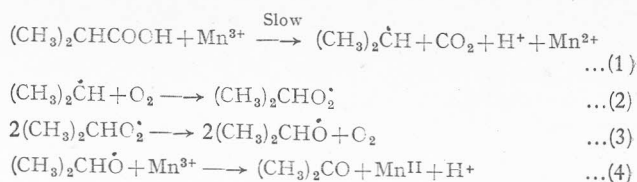
Fig. 1 — Rate plots for Mn^{3+}-isobutyric acid (IBA) and Mn^{3+}-diglycolic acid (DGA) systems [(A) $-R_{Mn}$ versus $[Mn^{3+}]$; $[H^+]$ = 2·5M; μ = 2·6M; $[IBA]$ = 0·4042M; temperature 40°. (B) k' versus $[IBA]$; $[H^+]$ = 2·5M; μ = 2·6M; $[MTA]$ = 0·004M; temperature = 45°. (C) k' versus $[DGA]$; $[H^+]$ = 2·5M; μ = 2·6M; $[MTA]$ = 0·004M; temperature = 30°]

$$(CH_3)_2CHCOOH + Mn^{3+} \xrightarrow{Slow} (CH_3)_2\dot{C}H + CO_2 + H^+ + Mn^{2+} \quad \ldots(1)$$

$$(CH_3)_2\dot{C}H + O_2 \longrightarrow (CH_3)_2CHO_2^{\cdot} \quad \ldots(2)$$

$$2(CH_3)_2CHO_2^{\cdot} \longrightarrow 2(CH_3)_2CH\dot{O} + O_2 \quad \ldots(3)$$

$$(CH_3)_2CH\dot{O} + Mn^{3+} \longrightarrow (CH_3)_2CO + Mn^{II} + H^+ \quad \ldots(4)$$

Scheme 1

Scheme 2

metry is two and hence the rate should be unaffected by O_2, as observed.

Manganese(III) acetate + diglycolic acid system — The product analysis showed the formation of formaldehyde as one of the products. The stoichiometry calculated by taking excess $[Mn^{3+}]$ and titrating the remaining $[Mn^{3+}]$ after the completion of reaction shows $-\Delta[Mn^{3+}]/-\Delta[DGA] = 2$. The absence of any change in the spectrum of Mn^{3+} after the addition of diglycolic acid indicates the outersphere mechanism. The mechanism proposed is shown in Scheme 2.

A similar mechanism was proposed in Co^{3+}-diglycolic acid system[7] and v^{5+}-diglycolic acid system[8].

The similar mechanism for both systems is further supported by the same free energy of activation value ($\Delta G^{\ddagger} = 22.5 \pm 1.0$ kcal). The high positive entropy of activation ($\Delta S^{\ddagger} = 22.9$ e.u. for Mn^{3+}-isobutyric acid and $\Delta S^{\ddagger} = 5.0$ e.u. for Mn^{3+}-diglycolic acid system) also provides evidence for the outersphere mechanism because most of the reactions which follow innersphere interaction give negative $\Delta S^{\ddagger}$ value. The energy of activation (E_a) values for Mn^{3+}-DGA and Mn^{3+}-IBA systems are 24·0 and 31·0 kcal/mol respectively.

rate constants, k' were calculated. Plots of k' vs $[substrate]_0$ being linear and passing through the origin indicated that the reaction with respect to $[substrate]$ followed first order kinetics (Fig. 1). The pseudo unimolecular constants (k') for the system Mn^{3+}-DGA at 20°, 25° and 30° are 12·37, 26·79 and 46·84×10⁻⁵ (sec⁻¹) respectively and those for Mn^{3+}-IBA system at 35°, 40° and 45° are 9·19, 16·1 and 43·5×10⁻⁵ (sec⁻¹) respectively.
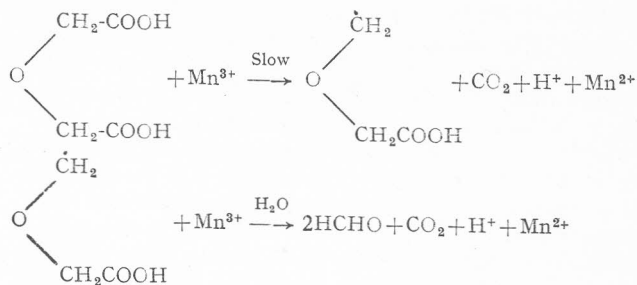
The variations of $[Mn^{3+}]$, $[H^+]$ and μ has no effect on the rates. Rapid initiation of polymerization indicates free radical mechanism for both the systems.

Manganese(III) acetate + isobutyric acid system — The test for formic acid was negative, thereby eliminating its formation in this system. The presence of acetone was confirmed by co-TLC of the 2,4-dinitrophenylhydrozone. No difference in rate was observed under air or nitrogen atmosphere. No change in the spectrum of manganese(III) acetate immediately after the addition of isobutyric acid was observed. The mechanism which suits well for the above results is shown in Scheme 1.

Reactions (1) to (4) operate in aerobic conditions. The stoichiometry ($-\Delta[Mn^{3+}]/-\Delta[IBA]$) for the above mechanism is two. Under anaerobic condition Wells *et al.*[3] observed the product to be isopropyl alcohol instead of acetone. Here also the stoichio-

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