

manganese (II) acetate was found spectrophotometrically. The overall rates of polymerization were measured at different temperatures and the energy of activation was computed.

Manganese (III) acetate is a fairly good initiator causing a 25% conversion in 20 minutes at 40°C. The rate of polymerization of acrylamide was found to be directly proportional to the monomer concentration (*vide* Fig. 1). Another salient feature of this system

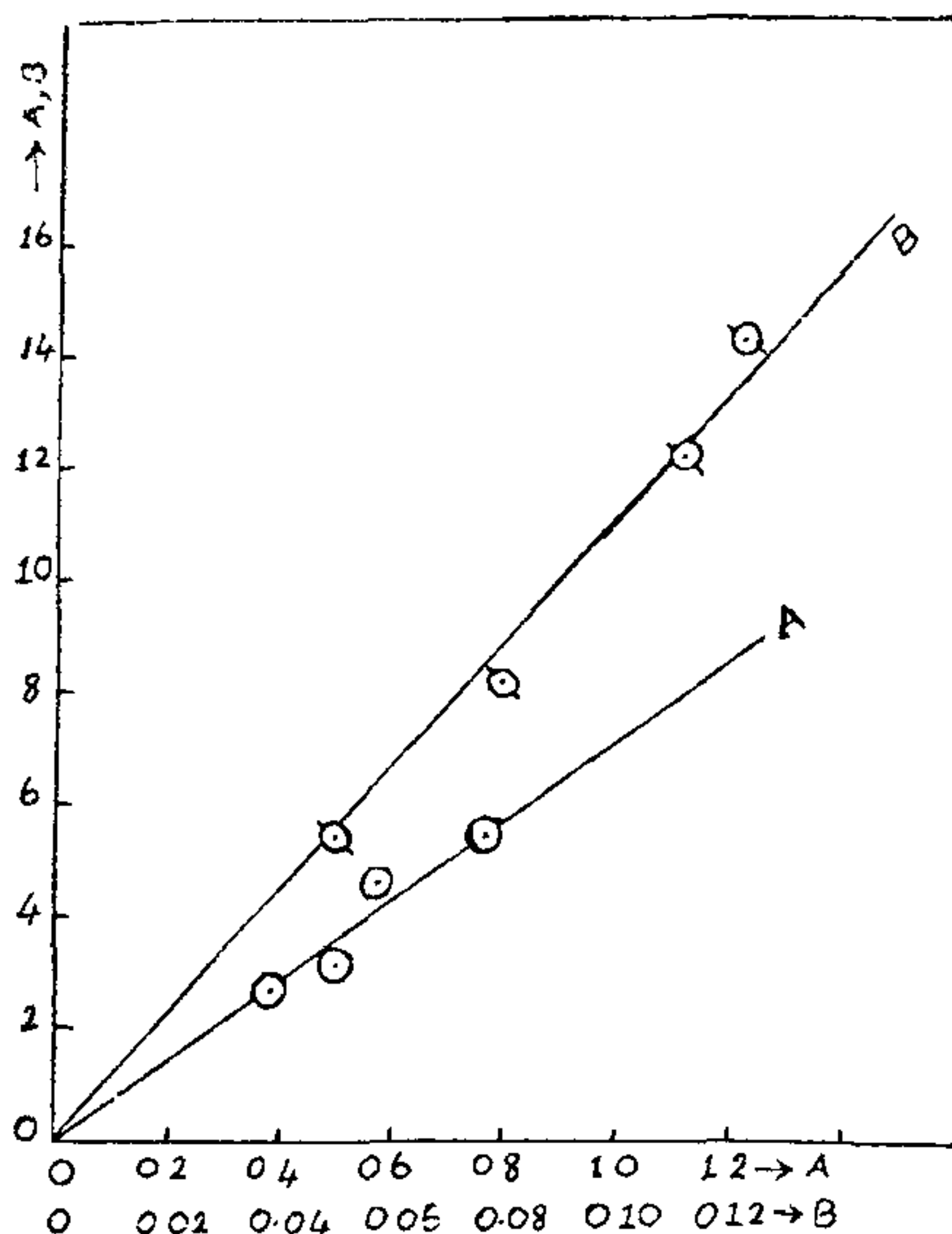
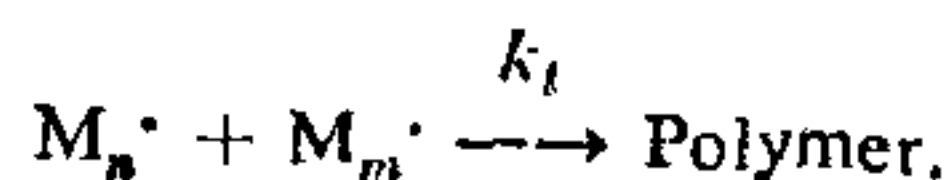
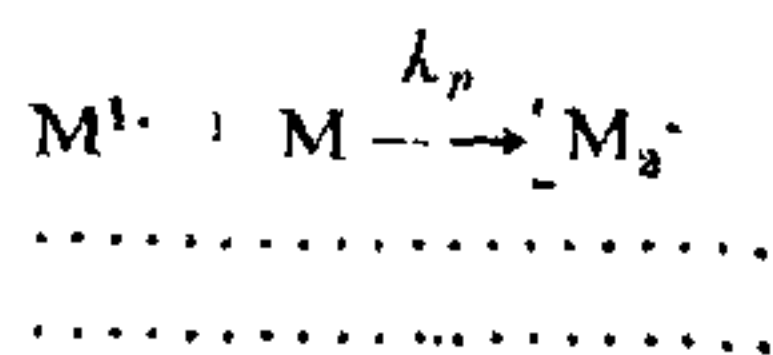
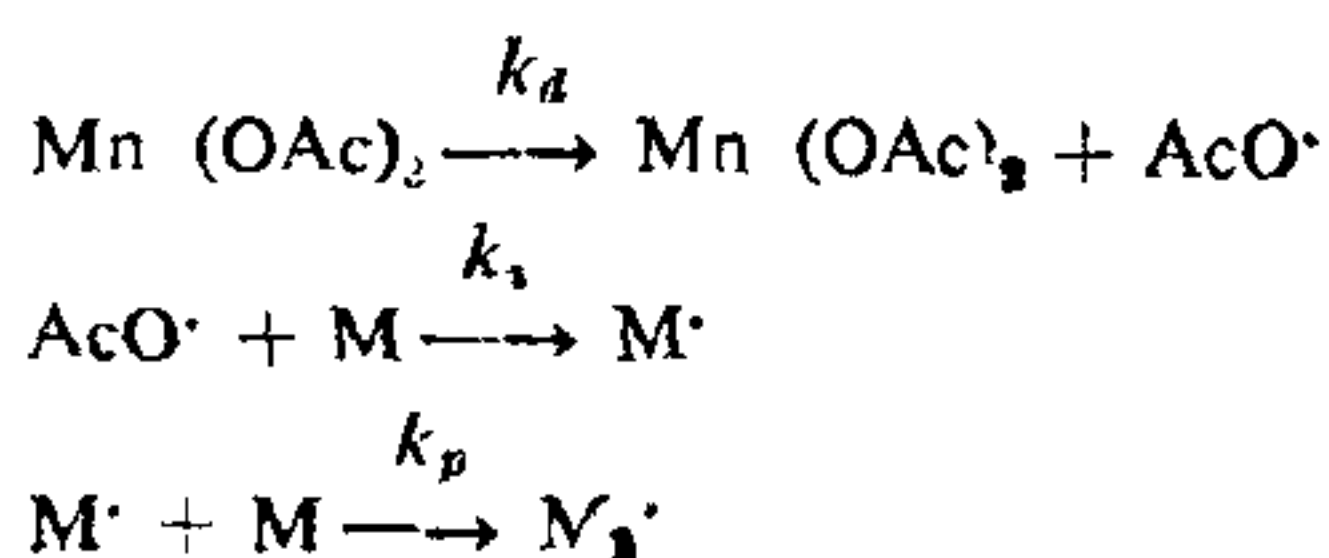


FIG. 1. Effect of monomer concentration and metal concentration on rates.  $T = 40^\circ\text{C}$ ,  $t = 25$  minutes. A,  $-d[M]/dt \times 10^6 \text{ Vs } [M]$ , B,  $-d[M]/dt \times 10^6 \text{ Vs } [\text{Mn(III)}]^{1/2}$ .

is that it conforms to the ideal system where the rate of polymerization of acrylamide is proportional to half the power of the initiator (*vide* Fig. 1). The overall energy of activation is 13.9 kcal/mole suggesting that the polymerization is by free radical mechanism since for ionic polymerization the energy of activation will be very low. This suggests that manganese(III) acetate decomposes to manganese(II) acetate and acetate radical ( $\text{CH}_3\text{COO}^\cdot$ ). The decomposition of  $\text{Ti(III) acetate}$  and initiation by acetate radical was already proposed<sup>3</sup>. Mutual termination of chain radicals is postulated to explain the kinetics.



Assuming the steady state conditions and assuming  $k_p$  and  $k_t$  to remain constant and independent of chain length, the following expressions are derived:

$$-d[M]/dt = k_p/k_t^{1/2} k_d^{1/2} [M] [I]^{1/2}$$

and

$$-d[I]/dt = k_d [I]$$

A similar behaviour was also observed in the thermal polymerization of methacrylamide initiated by manganese(III) acetate<sup>4</sup>. The rate constants calculated were

$$k_d = 2.10 \times 10^{-4} \text{ sec}^{-1}$$

and

$$k_p^2/k_t = 1.30 \times 10^{-4} \text{ liters/mole-sec.}$$

Manganese(III) acetate also initiates vinyl polymerization photochemically to a lesser extent. Further work is in progress with various other monomers to understand the kinetics and mechanism of polymerization.

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#### CHEMICAL CONSTITUENTS OF *LORANTHUS FALCATUS* LINN. f.

In a scheme to study and compare the chemical constituents of the host and the parasitic plants, the stems of *Loranthus falcatus* [Syn: *Dendrophoe falcatus* (Loranthaceae)]<sup>1</sup> growing on mango trees, were collected from Ananthagiri hills for investigation. It grows mostly in deciduous forests on the host plants such as acacias and mango trees. These are parasitic shrubs, whose astringent stem bark is reported to be narcotic; it is used locally as a cure for consumption and several other ailments<sup>1</sup>.

Only two related species, *L. grewiniki*<sup>2</sup> and *L. pentandrus*<sup>1</sup> were examined earlier. The former contained

lup-20(30)-en-3 $\beta$ , 7 $\beta$ -diol, loranthol, and the latter, quercitrin.

The alcoholic extract concentrate from the stems was fractionated successively into hexane, chloroform and methanol solubles. The hexane and chloroform extracts showed similar spots on TLC and the combined concentrate was separated on silica gel column by elution with hexane, hexane-benzene, benzene and benzene-ethylacetate.

The hexane and hexane-benzene (19:1) eluates gave rise to unidentified oils and plant alcohols. With hexane-benzene eluate (3:1)  $\beta$ -amyrin acetate was isolated and identified by hydrolysis to  $\beta$ -amyrin. In the next eluate of hexane-benzene (1:1), an apparently new triterpene,  $C_{33}H_{54}O_4$ , m.p. 219–220°,  $[\alpha]_D^{25} + 56^\circ$ , I.R. 1735  $cm^{-1}$  was isolated. Further elution with benzene and benzene-ethylacetate furnished  $\beta$ -sitosterol, stigmasterol and oleanolic acid. All the triterpenes and the plant sterols were identified with authentic samples (TLC, m.m.p. and I.R.).

The new triterpene showed no hydroxyl peak in I.R. but an ester carbonyl peak at 1735  $cm^{-1}$ . Its NMR spectrum in  $CDCl_3$  showed 7- $CH_3$  at  $\delta$  0.71–1.13, one acetoxymethyl at  $\delta$  2.05 (s) 3H, one carbomethoxyl at  $\delta$  3.63 (s) 3H,  $\alpha$ -hydrogen of acetoxyl at  $\delta$  4.6 (t) 1 H and one olefinic proton at  $\delta$  5.33 (m). From the above data, the triterpene can be regarded as a methyl ester acetate of a monohydroxy triterpene carboxylic acid. On hydrolysis with 5% methanolic KOH, a hydroxy methyl ester is secured as colourless irregular plates,  $C_{31}H_{50}O_3$ , m.p. 196°,  $[\alpha]_D^{25} + 70^\circ$ , I.R. 3450  $cm^{-1}$  and 1735  $cm^{-1}$ . In its NMR spectrum the acetoxyl protons were absent, but indicated one carbomethoxy at  $\delta$  3.65 (s) and olefinic protons at  $\delta$  5.33 (m) 1 H. By comparison (TLC, m.m.p. and I.R.) with authentic samples, the hydrolytic product and its parent triterpene were identified as oleanolic acid methyl ester and oleanolic acid methyl ester acetate respectively.

This appears to be first report of the occurrence of oleanolic acid as methyl ester acetate in nature. Oleanolic acid is known to occur frequently free and also as acetate<sup>3</sup>. In the host mango tree, *Mangifera indica*, triterpenes related to cycloartanol, namely mangiferolic acid, hydroxy mangiferonic acid<sup>4</sup> and a xanthone mangiferin<sup>5</sup>, have been reported.

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#### STUDIES ON MORPHOLINE-4 CARBODITHIOATE COMPLEX OF TELLURIUM(IV)

THE fungicidal active morpholine-4-carbodithioate chelate of tellurium(IV) is stable upto 160° and after that, it decomposes rapidly upto 300°. The i.r. spectra indicate the bidentate behaviour of the ligand in the chelate. The reagent precipitates tellurium (IV) quantitatively as yellow complex in pH range 3.5–6.5. Tellurium(IV) is determined by weighing the complex as  $Te(C_5H_8ONS_2)_4$  after drying at 110–120°. The reagent has also been used in the separation and determination of Te(IV) in the ternary mixture with Cu(II) and Ni(II). The interference due to Ni(II), Zn(II), Cd(II), Co(II), Fe(III), In(III) and Ga(III) ions have been avoided using ammoniacal EDTA and tartrate as masking agent.

A number of tellurium(IV) dithiocarbamates have been reported in literature<sup>1–6</sup>. Very little is known about quantitative estimation of Te(IV) with dithiocarbamates. Bayer and Ott<sup>6</sup> reported morpholine-4-carbodithioate as a possible analytical reagent. Though the reagent is not very much selective, it has been possible to determine tellurium(IV) by masking a number of metal ions using the mixture of ammoniacal EDTA and tartrate. In the present communication morpholine-4-carbodithioate is used as analytical reagent for the gravimetric determination of tellurium and separation of Te(IV), Cu(II) and Ni(II) from their ternary mixture, in addition to the fungicidal, thermogravimetric and i.r. spectral studies.

#### Materials and Method

The potassium salt of the reagent was prepared by mixing potassium hydroxide, morpholine and carbon disulphide in ether at 0° in a ratio 1:1:1. 1% (w/v) reagent solution was prepared in distilled water.

Potassium tellurite (Riedle) was dissolved in double distilled water to prepare the tellurium(IV) solution. The concentration was estimated by using the standard method<sup>7</sup>.

#### Isolation of the Complex

A known volume of the Te(IV) solution was diluted to 150 ml and heated to 40–50°. A four-fold excess of 1% (w/v) solution of the reagent was added and its pH was adjusted between 5.0–6.5. A bright yellow