CHAPTER - II

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EXPERIMENTAL TECHNIQUES

The oxidation of malonic acid, dimethyl malonate and diethyl malonate by Mn(III) acetate in acetic acid medium was studied here. In soultion, Mn(III) disproportionates to Mn(II) and Mn(IV) by the reaction,

$$2\ Mn(III) \rightleftharpoons Mn(II) + Mn(IV).$$

The reaction can be shifted to the left by using highly acidic medium. This can be done either by the use of glacial acetic acid medium or perchloric acid medium. Hence, we have used acetic acid medium throughout this investigation.

During the course of the reaction, Mn(III) is reduced to Mn(II). However, Mn(III) is strongly absorbing species (λ = 420 nm, ϵ = 250) as compared to Mn(II) which is practically non-absorbing at 420 nm. So the observed absorbance (A) at 420 nm may be safely taken as a measureof concentration of Mn(III) during the course of the reaction. Hence, in the present investigation reaction was followed photometrically at 420 nm wavelength.

2.1 PREPARATION OF Mn(III) ACETATE :

AR/GR quality chemicals were used for this preparation.

Glacial acetic acid (B.D.H.) was purified over chromium oxide and subsequent fractional distillation[44] . Christiansen's[8] method was used for the oxidation of Mn(II) acetate to Mn(III) acetate by potassium permanganate in presence of glacial acetic acid. For this, a mixture os unhydrous Mn(II) acetate (15.15 g) and glacial acetic acid (220 ml) was refluxed for about 2 hours. Potassium permanganate (3.41 g) was then added and mixture was again refluxed for another 45 minutes with constant stirring. The reaction mixture was cooled slowly and water (37.5 ml) was added dropwise with constant stirring during cooling process. The reaction mixture was stored in dark for 3 days whereby Mn(III) acetate was obtained as a crude product. The product was then dissolved in minimum quantity of hot mixture of glacial acetic acid and water (in the proportion 5:1). On cooling to room temperature, Mn(III) acetate dihydrate was obtained as fine crystals. The product was then filtered and dried under vaccum.

2.2 PURITY OF THE CHEMICALS :

All the chemicals used during investigation were of AR/GR or equivalent quality. Malonic acid, dimethyl malonate and diethyl malonate were supplied by Riedel. Their purity was checked by determining the m.p. of malonic acid (136°C),

the B.P.' of dimethyl malonate (180°C) and diethyl malonate (199°C)[45] . The other chemicals used (sodium thiosulphate, potassium iodide, acrylonitrile, etc) were supplied by B.D.H.

2.3 PREPARATION OF SOLUTIONS :

Stock solutions of Mn(III) acetate (0.01 M), malonic acid (0.1 M), dimethyl malonate (0.5 M) and diethyl malonate (1.98 M) were prepared by weighing the required quantity of the reagent and dissolving it in glacial acetic acid. The solutions were stored in dark. The glassware used for preparing and storing the solutions was of pyrex glass. Strength of Mn(III) acetate stock solution was checked periodically by use of iodometric method . For this, 2 ml stock solution of Mn(III) acetate (0.01 M) was taken in iodine flask, 10 ml of KI (5%) and 3 drops of 2 N H_2SO_4 solution were added to it. The liberated iodine was titrated against 0.001 M. Sodiumthiosulphate solution by using starch as an indicator, from which normality of Mn(III) acetate was determined. It was used for the further calculations.

2.4 DETERMINATION OF λ_{max}.FOR Mn(III) ACETATE :

2×10^{-3} M solution of Mn(III) acetate was prepared in glacial acetic acid. Absorbance of this solution was

measured as a function of wavelength in range of 400-700 nm. Glacial acetic acid was used as a reference. Measurements were done on SPEKOL, wave length 350 nm to 850 nm. CARL ZEISS JENA, made in GERMANY DDR, 734035. The graphe of Absorbance (A) versus wavelength (nm) is shown in Fig.1 . It is seen that Mn(III) acetate has a strong absorption at 420 nm.

2.5 FOLLOWING THE KINETICS :

All the kinetic measurements were carried out in pyrex glassware which was coated outside with Japan black to avoid photochemical effects particularly on Mn(III) acetate. 25-30 ml of stock solutions of Mn(III) acetate, the organic substrate (Malonic acid, Dimethyl malonate etc) and glacial acetic acid were kept in separate well stoppered bottles/ iodine flasks and equilibrated to the required temperature in a thermostat (BIJOU made in India) for about 15-20 minutes. The required volumes of these solutions were mixed in an iodine flask (Total volume of the solution 50 ml) and absorbance (A) of the reaction mixture at 420 nm was measured at definite time intervals by pipetting out 2 ml of the reaction mixture at each time. A reference solution contained all the other reactants except Mn(III) acetate.

The reaction was usually followed upto 80% completion. This data was then used to calculate (-dc/dt), velocits constants etc. The following variations were studied -

1) Variation of concentration of Mn(III) acetate.
2) Variation of substrate concentration.
3) Variation of water concentration.
4) Variation of temperature of the experiment.

The observations, graphs and results are given and discussed in Chapter - III, IV and V.

FIG. 1 — DETERMINATION OF λ_{max}.

PLOT OF OPTICAL DENSITY VERSUS WAVELENGTH.