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THERMAL ANALYSIS APPLIED TO CHLOROMYCETIN PRODUCTS

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Studies have been made on the physicochemical processes in heat treating chloromycetin semifinished products, and optimum conditions have been defined for heat treatment and drying.

Thermal analysis is increasingly applied to the physical and chemical processes in drying materials [1] because modern instruments provide improved resolving power and new approaches have been devised providing for quantitative results in drying kinetics and mechanisms [2].

Particular interest is attached to determining transition temperatures related to water removal and reactions, since this enables one to forecast the best temperatures for heat treatment and drying and to determine thermal effects accompanying the processes, as well as thermophysical characteristics.

We have used an MOM derivative recorder made in Hungary [3] to examine the physicochemical processes in treating synthetic broad-spectrum antibiotics: chloromycetin and semifinished products from it: threoamin, levoamin, an oxymethyl compound, and dextramin. Figures 1-4 show the recordings. The masses were 400-680 mg, heating temperatures not more than 250°C, heating rates 2.5-10°C/min, sensitivity in TG curve recording 200 mg, DTA and DTG 1/15. Oven atmosphere was air. All the experiments were performed with open ceramic crucibles.

Figure 1a shows that chloromycetin has three effects, peaks at t = 75-110, 140-150, 175°C and above in accordance with the heating rate. The effect at 75-110°C is due to free-water loss. The mass loss in the range 25-110°C lasts for 15 to 40 min, during which up to 30% of the water is lost, which coincides with the initial water content determined by the vapor-pressure method. The subsequent effects characterize the individual features.

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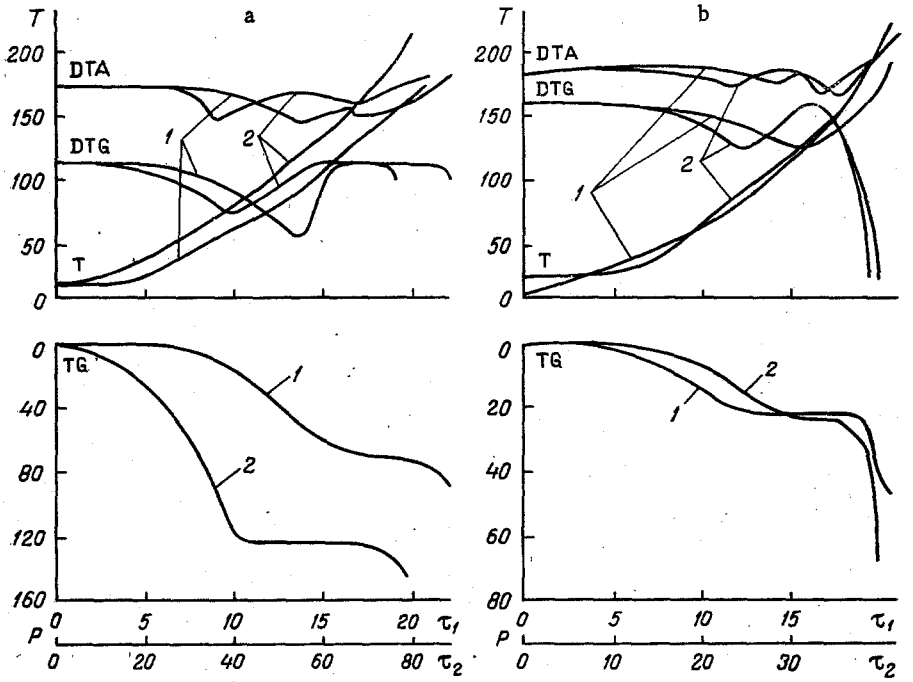

Fig. 1. Thermograms for chloromycetin and semifinished products: a) chloromycetin (m_0 = 400 mg): 1) g = 10°C/min; 2) 2.5; b) threoamin (m_0 = 420 mg): 1) g = 10°C/min; 2) 5.

The parameters of chloromycetin [4] show that the effect at t = 140-150°C is due to melting, which is accompanied by change in heating rate without mass loss. The third effect is accompanied by a sharp mass loss with considerable heat production, where burning occurs, as is evident from the appearance at the end.

When the heating rate is increased, the water evaporation and the physicochemical reactions in the chloromycetin occur at higher temperatures over shorter intervals. At 10°C/min, the drying is complete in 15 min at 107°C, i.e., 2.6 times more rapidly than at 2.5°C/min. The decomposition, melting, and ignition temperatures are correspondingly raised by 10-20°C.

These physicochemical transformations enable one to forecast the behavior and thus to choose drying methods and working parameters. For example, the classification [1] shows that the optimum drying conditions for chloromycetin having W = 10-15% are an inlet air temperature of 120-130°C, material temperature 85-95°C, treatment time not more than 10-15 min, and heating rate not more than 10°C/min.

Figure 1b shows threoamin behavior; we used it dry and moistened with water. It is evident from Fig. 1b that it resembles chloromycetin in having three effects at t = 75-110, 140-150 and 150-170°C and above. The first is accompanied by mass loss due to removal of water, as was confirmed from the drying kinetics under isothermal conditions (Fig. 2). The others are due to decomposition, melting, and distillation. There is marked mass loss, and much heat is absorbed. Threoamin becomes yellow at 90°C. The temperature should thus not exceed 90°C and the treatment time 8-10 min at 10°C/min. The entering air temperature should not be more than 110°C.

Figure 3 shows similar thermograms for levoamin. The first effect is due to water loss, time dependent on heating rate, since at 2.5°C/min it was 30-32 min and terminated at 75°C, while at 10°C/min, the rate was increased by more than a factor two and the loss ended at t = 100-110°C. The rate also influences the decomposition and combustion. At 2.5°C/min, it begins to decompose at 135-137°C, while increasing the rate by a factor of four raises the decomposition point by 10-20°C. There is rapid mass loss and heat is produced during the combustion. Ignition at 10°C/min occurs at 160-166°C, which is 10-14°C above the data of [4], evidently due to the different conditions.

The optimum drying conditions require rapid water removal at 80-90°C, while the incoming air temperature can be kept 5-10°C below the decomposition point if the process is stringently controlled.

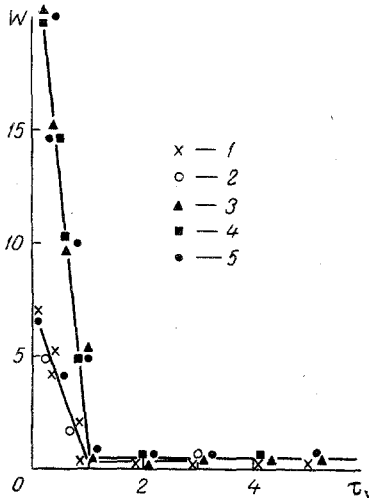

Fig. 2. Drying kinetics under isothermal conditions (T = 105°C): 1) chloromycetin; 2) oxymethyl compound; 3) threoamin; 4) dextramin; 5) levoamin; τ in h.

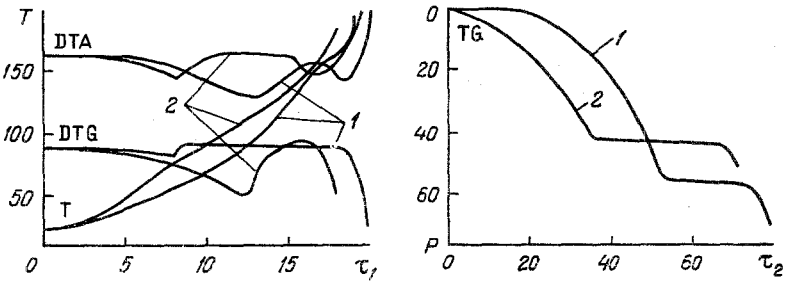

Fig. 3. Thermograms for levoamin (m_0 = 400 mg): 1) g = 10°C/min; 2) 2.5.

We also examined an oxymethyl compound and dextramin (Fig. 4).

The oxymethyl compound has three effects at 75-95, 150-175, 180°C and above in accordance with the heating rate (Fig. 4a), which correspond to drying, decomposition, and melting [4]. Heat is absorbed to an extent dependent on the heating rate. The following drying conditions are recommended: incoming air temperature 120-140°C, material at 80-90°C, drying 5-8 min.

Figure 4b shows the dextramin results. There are three prominent effects, the first due to water loss. At 5°C/min, this lasts 22.5 min and terminates at 97°C, and then there is a rapid temperature rise without phase change. At 150°C, the heating rate alters and there is mass loss, accompanied by an endothermic effect. The thermogram and the classification [1] indicate an optimum rate of 5°C/min for drying with an incoming air temperature of 120-130°C and the material at 85-100°C. Processing gives the water content as a function of temperature and heating rate as a regression equation:

$$u = \sum_{i=1}^{n} c_i \tau_i = \sum_{i=1}^{n} c_i \left(\frac{t_i}{g_i} \right)^i. \tag{1}$$

The temperature dependence of the water content gives the rate constant for water loss (drying coefficient):

$$\frac{du}{1 - \frac{u}{u_\infty}} \frac{1}{u_\infty} = \frac{k}{g} dt. \tag{2}$$

The drying kinetics under dynamic conditions enable one to relate the mass flux density to the drying rate:

$$g_m = \rho_c R_v \frac{du}{d\tau}, \tag{3}$$

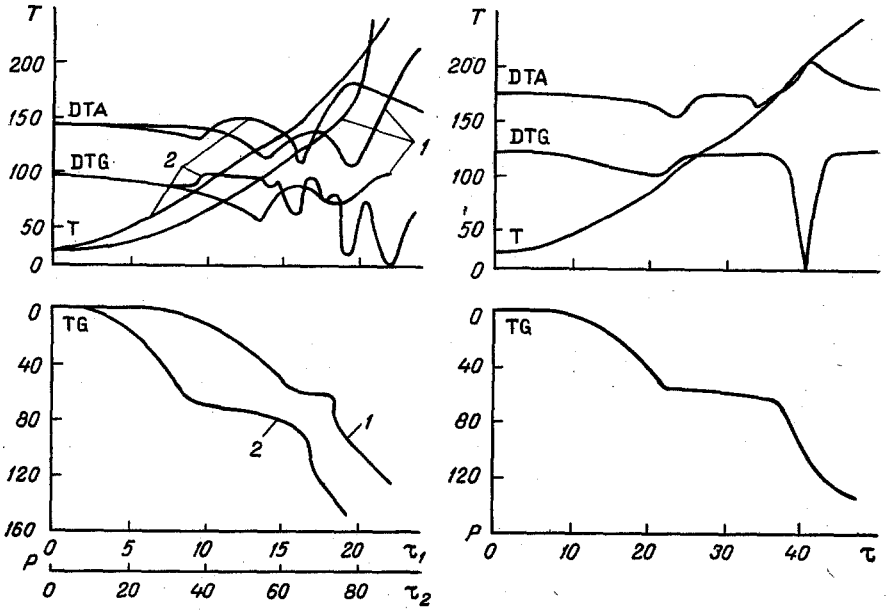

Fig. 4. Thermograms for chloromycetin semifinished products: a) oxymethyl compound (m_0 = 680 mg): 1) g = 10°C/min; 2) 5; b) dextramin (m_0 = 500 mg, g = 5°C/min).

and to determine the subkinetic parameters

$$\frac{d^2u}{d\tau^2}, \quad \frac{d^2t}{d\tau^2}, \quad \frac{d^2t}{du^2},$$

which characterize the drying acceleration (similar to the acceleration in mechanical motion), i.e., the rate of reduction in the drying rate in the second period or the rate at which the water content approaches the equilibrium value.

These kinetic parameters are needed in calculations on drying and heat treatment for any preset conditions.

These thermal data provide the following: 1) individual parameters and the physicochemical transformations on heating, which may be accompanied by heat production or absorption, and the temperature ranges and times where various effects are attained; 2) the weight loss kinetics; 3) forecasts for drying methods and parameters; and 4) use for simulating heat treatment.

NOTATION

t, temperature, °C; W, water content, %; u, specific water content; c_i, regression coefficients; τ, heat-treatment time, min; g, heating rate, °C/min; k, drying coefficient; m_0, mass used, mg; ρ, density of dry material, kg/m^3; R_V, geometrical factor (R_V = V/F); V, body volume, m^3; F, evaporation surface, m^2.

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