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THE THERMAL DECOMPOSITION OF GUM TRAGACANTH IN NITROGEN

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ABSTRACT

The thermal degradation of gum tragacanth in nitrogen has been studied by thermogravimetric (TG) and isothermal mass-loss methods. In TG experiments the total mass-loss at 700°C was 75%. It has been shown that the TG characteristics were not affected by particle size variation. The isothermal decomposition data carried out at five different temperatures in the range between 185 and 206°C fitted a Prout and Tompkins equation but a good fit was also obtained for a contracting sphere based equation. The physical mechanics of degradation of the gum tragacanth have been interpreted on the speculation that it is initiated through the formation of planes of lateral strain which are sites for decomposition and which decrease inversely with time. An activation energy of about 150 kJ mole^{-1} has been found for the degradation of gum tragacanth from the calculations based on the results of isothermal data.

INTRODUCTION

Gum tragacanth is the exudate of the plant genus *Astragalus*. This is a small shrub with a large tap root which is tapped for the gum along its branches [1]. It has been used for medical purposes for a long time and is especially cultivated as a crop in Iran. It occurs in ribbons and flake form. It is most commonly used in the form of ribbons and seldom used in powdered form since the milling process required reduces its thickening capacity.

Gum tragacanth (GT) has a complex structure not completely elucidated. It has, however, been shown that GT is a mixture of polysaccharides consisting of three main components, namely a neutral polysaccharide, tragacanthic acid and a third component thought to be a glucoside [2]. GT polysaccharides are branched polymers consisting of main chains of an α-D-galacluronic acid residue united to 1,4-α-glycosidic linkages. To this main chain are attached residues of monosugars in terminal and intermediate positions.

This high hydroxyl containing branched polymer absorbs large quantities of water and produces highly viscous hydrocolloid solutions.

Zahedi et al. [3] consider particle size variations as an important factor in determining the final viscosity of the gum hydrocolloid solutions. The purpose of the present study is to evaluate the thermogravimetric behaviour of GT and to establish the effect of GT size reduction on thermogravimetric behaviour.

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EXPERIMENTAL

A commercial sample of Iranian gum tragacanth ribbon (GTR_3) was supplied by the Institute of Standard and Industrial Research of Iran (ISIRI).

A Glen Creston microhammer mill, type ΔFH48, was used for grinding and an Endecott vibrating sieve, model E.F.L., for gum powder classification.

The thermal degradation was observed in terms of mass-loss by using a Stanton Redcroft Thermobalance, model TG 750. An atmosphere of dry nitrogen was passed into the furnace at a flow rate of 50 ml min^{-1}.

Both the thermogravimetric (TG) experiments and the isothermal heat treatments involved weighing the sample into a crucible which was placed on the thermobalance. In the TG experiments, the furnace was raised, the balance mechanism was released, and after allowing 15 min for nitrogen to purge the system, the temperature was increased to 700°C at a rate of 5°C min^{-1}. In the isothermal experiments, the temperature was raised by 5°C min^{-1}, kept constant for 30 min at the appropriate temperature to eliminate the sorbed water and then raised very rapidly to the desired temperature. The mass-loss was then recorded by reference back to the mass-loss at the end of the plateau representing the loss of sorbed water.

RESULTS AND DISCUSSION

Typical thermogravimetric curves obtained for the degradation of GT at various particle size fractions are shown in Fig. 1 as percentage mass-loss against temperature. The first mass-loss occurred in the temperature range 0–225°C with a total mass-loss of 15%. This loss is attributable to the evaporation of sorbed water from

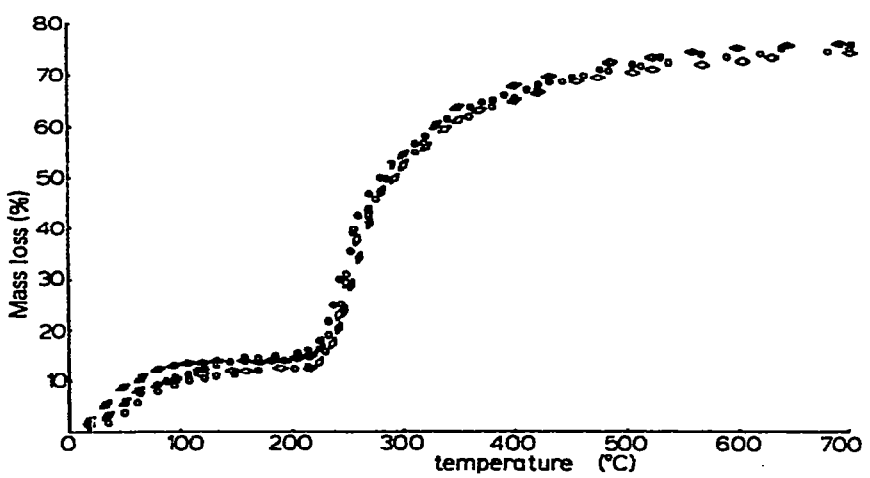

Fig. 1. Thermogravimetric curves of gum tragacanth (Ribbon 3) in nitrogen showing the mass percent loss against temperature (°C) for a 10 mg sample with a heating rate of 5°C min^{-1}. Particle size (μm):◆, $500<r<1000$;◇, $250<r<500$; ●, $75<r<250$;○ $r<75$.

GT. The smaller the particle size, the faster the rate of desorption. This could be explained on the basis that mass-loss is a function of the increased area consequent upon particle size reduction. The second and major mass-loss for all four samples began at 225°C. This corresponded to 60% of the initial sample mass. The decomposition of all samples was rapid up to 400°C before tailing off to a very slow mass-loss which was still in evidence at 700°C. The total mass-loss at 700°C was 75% of the initial sample mass.

Considering the chemical structure of GT, i.e. a highly hydroxylated branch polymer, and the tragacanthic acid as its main constituents, it would seem possible to attribute the second mass-loss to the hydroxylated polysaccharide decomposition. Figure 1 also suggests that the samples of different particle size have no major differences in the second mass-loss region. The kinetics of the thermal degradation of the GTR_3 ($r > 500\ \mu m$) may therefore be examined in some detail as an example of the manner in which all the samples degrade.

KINETICS OF DEGRADATION

Isothermal mass-change determinations were carried out on GT in dry nitrogen at temperatures between 185 and 206°C. The results of experiments carried out at 185, 190, 195, 200 and 206°C are shown in Fig. 2 as percentage mass-loss against time of heating.

The technique already outlined,of bringing the gum tragacanth to the temperature of 172°C at a rate of 5°C min^{-1}, keeping it constant for 30 min, and then raising it very quickly to the desired temperature meant that the sorbed water forming the first mass-loss in the TG curve (Fig. 1) was eliminated and the second mass-loss region is the only stage remaining to be studied. However, the loss of further water (called

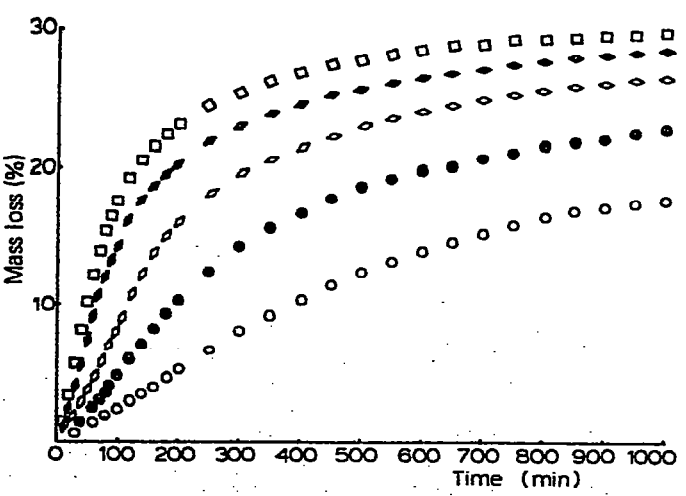

Fig. 2. Plots of mass-loss against time for isothermal degradation of gum tragacanth (Ribbon 3) in nitrogen. ○, 185°C; ●, 190°C; ◇, 195°C; ◆, 200°C; □, 206°C.

here combined water) amounted to 32% of the second stage. The total percentage mass-loss (Mt) in this second stage at any temperature was determined by allowing the run to continue for over 16 h and constructing a graph of mass-loss against reciprocal time, extrapolating it to $1/t = 0$ in order to estimate Mt. This proved to give a satisfactory straight line at each temperature. Plots of this kind for the data presented in Fig. 2 are shown in Fig. 3.

The data for each curve (Fig. 2) were plotted in the standard kinetic form [4] (Fig. 4) as degree of decomposition α, against reduced time, $t/t_{0.5}$, where α is the mass-loss at time t divided by total mass-loss and $t_{0.5}$ is the time when $\alpha = 0.5$. When plotted in this way, the data fitted a common curve at any temperature.

Analysis of the kinetic data show that the data fits a Prout and Tompkins [5] equation of the type

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = n \ln t + C \tag{1}$$

Figure 5 shows that derived plots of $\ln[\alpha/(1-\alpha)]$ against $\ln t$, in every case investigated, give straight lines, the slope and intercept of which represent n and c, respectively.

Equation (1) can be simplified to give

$$\left(\frac{\alpha}{1-\alpha}\right) = kt^n$$

or

$$\left(\frac{\alpha}{1-\alpha}\right)^{1/n} = kt \tag{2}$$

or

$$\frac{d\alpha}{dt} = K(1-\alpha)^{-2}\left(\frac{\alpha}{1-\alpha}\right)^{(1/n)-1} \tag{3}$$

where $n = 1.43$

Plots of $[\alpha/(1-\alpha)]^{0.7}$ against t for isothermal degradation of gum tragacanth (Ribbon 3) are linear for values of $\alpha = 0$–0.6 and this is shown in Fig. 6. From eqn.

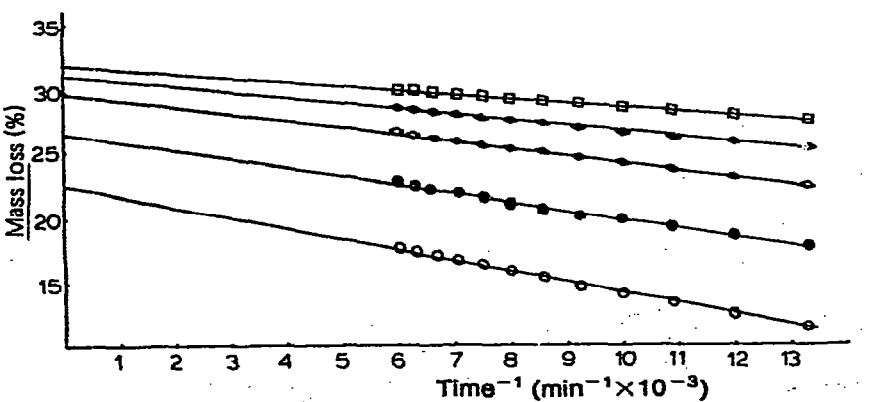

Fig. 3. Plots of mass-loss against reciprocal time for data presented in Fig. 2.

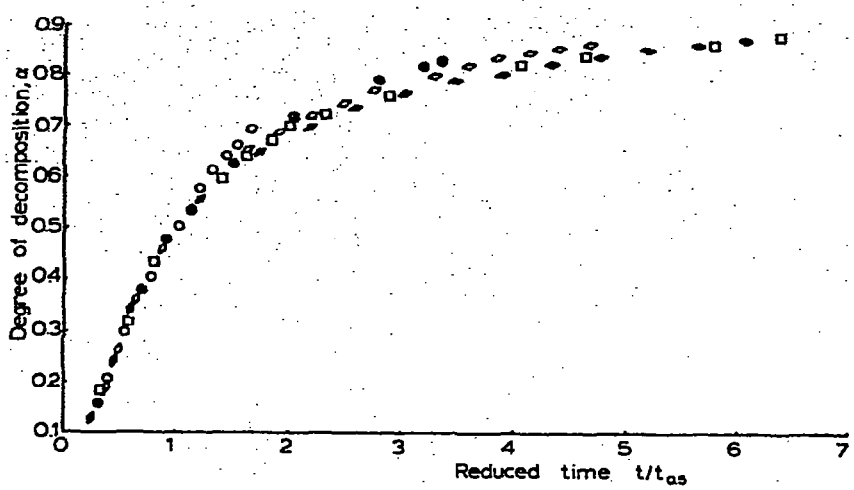

Fig. 4. Reduced time plot of the isothermal degradation of gum tragacanth (Ribbon 3) in nitrogen. ○, 185°C; ● 190°C; ◇, 195°C; ◆, 200°C; □, 206°C.

(2) it can be seen that the gradient of the $[\alpha/(1-\alpha)]^{0.7}$ against t plot is the rate constant k for the degradation at that temperature.

However, the isothermal decomposition of gum tragacanth may also be expressed

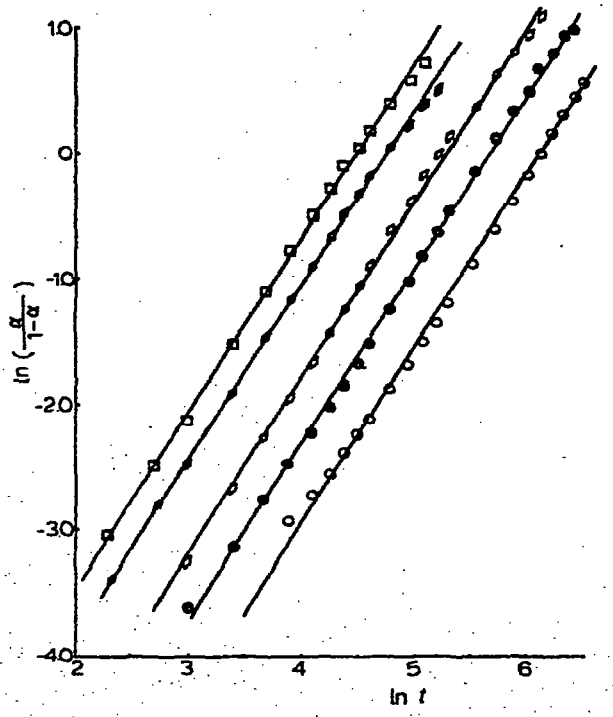

Fig. 5. Plots of $\ln[\alpha/(1-\alpha)]$ against $\ln t$ for isothermal degradation of gum tragacanth (Ribbon 3) in nitrogen. ○, 185°C; ●, 190°C; ◇, 195°C; ◆, 200°C; □, 206°C.

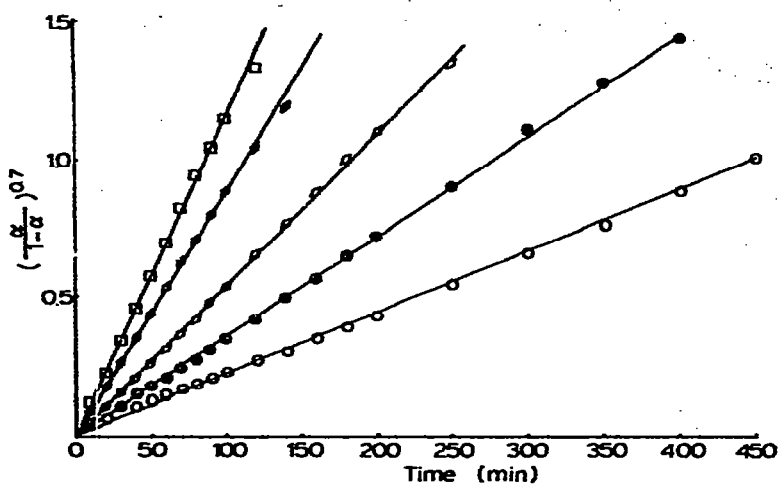

Fig. 6. Plots of $[\alpha/(1-\alpha)]^{0.7}$ against time for isothermal degradation of gum tragacanth (Ribbon 3) in nitrogen. ○, 185°C; ●, 190°C; ◇, 195°C; ◆, 200°C; □, 206°C.

by an equation of the type

$$1-(1-\alpha)^{1/3}=k't \tag{4}$$

or

$$\frac{d\alpha}{dt}=3K'(1-\alpha)^{2/3} \tag{5}$$

and linear plots were obtained for the decomposition data when these were plotted as $[1-(1-\alpha)^{1/3}]$ against time and are shown in Fig. 7.

The application of the Arrhenius equation, i.e.

$$K=A\exp(-E/RT)$$

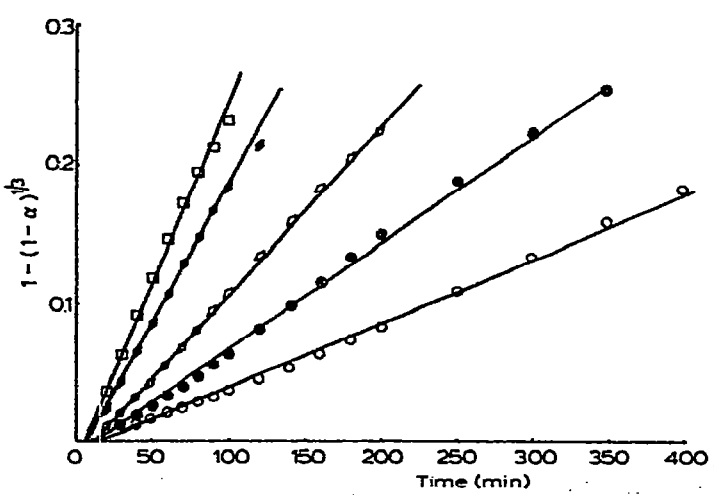

Fig. 7. Plots of $[1-(1-\alpha)^{1/3}]$ against time for isothermal degradation of gum tragacanth (Ribbon 3) in nitrogen. ○, 185°C; ●, 190°C; ◇, 195°C; ◆, 200°C; □, 206°C.

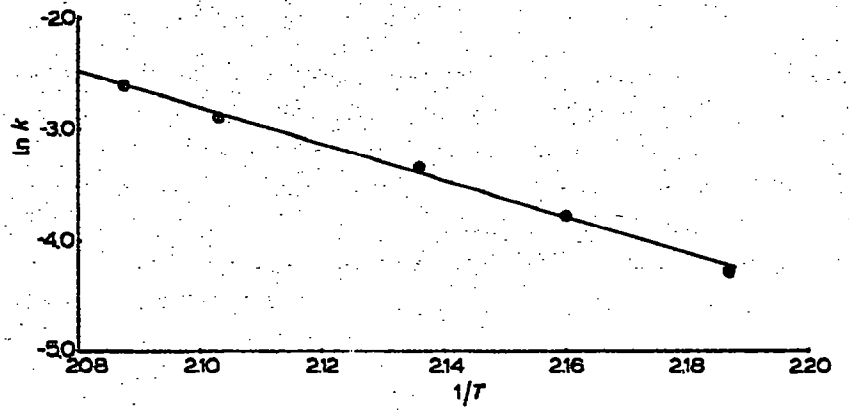

Fig. 8. Arrhenius plot of ln k against $1/T$ for the thermal degradation of gum tragacanth (Ribbon 3) in nitrogen.

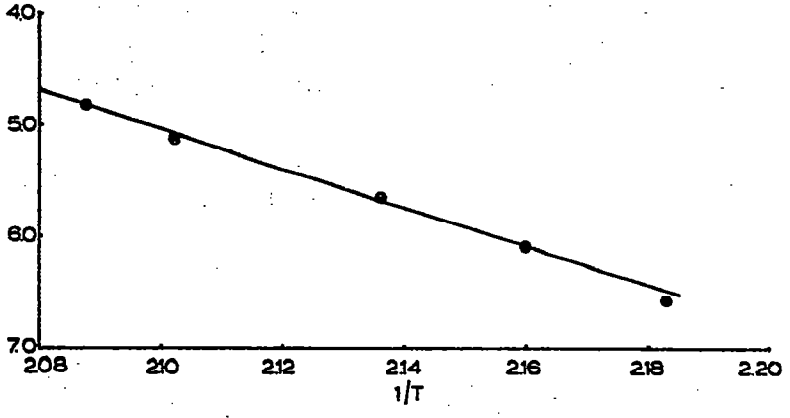

Fig. 9. Arrhenius plot of ln K' against $1/T$ for the thermal degradation of gum tragacanth (RIbbon 3) in nitrogen.

TABLE 1

The value for the activation energy calculated from rate constant obtained using eqn. (3)

T_C^0	$T_K^{-1}\times10^3$	ln K	Slope $-E/R$	E (kJ mole^{-1})	$A\times10^{-14}$	X intercept $\times10^3$	Standard deviation
185	2.1834	−4.2287					
190	2.15982	−3.76936					
195	2.13675	−3.3593	17941.9	149.175	15.3913	1.9500	0.043706
200	2.11417	−2.8973					
206	2.0877	−2.6173					

TABLE 2

The value for the activation energy calculated from rate constant obtained using eqn. (5)

T_C^0	$T_K^{-1}\times10^3$	ln K	Slope $-E/R$	E (kJ mole^{-1})	$A\times10^{-14}$	X intercept $\times10^3$	Standard deviation
185	2.1834	−6.577					
190	2.1598	−6.081					
195	2.13675	−5.638	18737.7	155.79	8.5442	1.838	0.07781
200	2.11416	−5.1194					
206	2.08768	−4.830					

where K is the rate constant, E is the activation energy, R is the gas constant and T is the isothermal temperature in Kelvin, allows the activation energy to be calculated. Plots of ln K and ln K' against $1/T$ are linear and shown in Fig. 8 and 9, respectively. The values of the activation energy calculated from the slopes of plots presented in Figs. 6 and 7 are given in Tables 1 and 2.

The value of activation energy obtained for thermal degradation of gum tragacanth using eqn. (3), 149.2 kJ mole^{-1}, is in good agreement with that obtained using eqn. (5), 155.8 kJ mole^{-1}.

SUMMARY AND CONCLUSIONS

The Prout–Tompkins equation is valid for situations where, in the acceleratory period, the surface array of product molecules produces lateral strains, which are relieved by cracks where nucleus formation is favoured and decomposition proceeds preferentially. Repetition of the process in the cracks may, according to this model, indicate branching deformation planes which later interfere as they reach surfaces at which decomposition has already occurred. The theory is applicable to decomposition of the type

Solid $\rightarrow$ solid + gas

provided that the molecular chains are absent.

Prout and Tompkins applied their theory to inorganic solids and implications inherent in their original equation, together with the condition that the molecular chains should not be present, imply that during an ensuing reaction the number of activated sites decreases exponentially. In the present study, while the applicability of eqn. (2) would suggest that a mechanism similar to that proposed by Prout and Tompkins exists, there are fixed number of sites, generated at the instant decomposition begins, which then decrease in number inversely proportional to time. However, the condition that chains should be absent needs some speculative comment. It must first be pointed out that the model proposed by Prout and Tompkins and utilised mainly in inorganic decomposition studies is not unique and a similar equation may possibly be derived on the basis of some other hypothesis. The identification of chains as molecular may not be necessary and the chain in fact could be a line or route along which decomposition can progress. For some kind of restrictive element leading progressively to a slowing down of the degradation process there must occur in this pathway some obstruction to offer hindrance at several places and thus an interrupted chain of this kind would be absent. This hindrance could arise in a number of ways, possibly by the advent of the initial dehydration process which preceeds the degradation stage kinetically analysed in this study. It should be noted that kinetic behaviour of this kind has been recorded for the pyrolysis of bark which is cellulosic in nature and has certain structural features in common with gum tragacanth [6].

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