

The Kinetics of the Thermal Degradation of the Synthetic Styrenated Polyester, Laminac 4116*

DAVID A. ANDERSON and ELI S. FREEMAN

Pyrotechnics Chemical Research Laboratory, Picatinny Arsenal, Dover, New Jersey

INTRODUCTION

Conventionally, the kinetics of the thermal degradation of polymers are studied by measuring rates of change in physical properties such as weight^{1,2} or viscosity³ over a series of constant temperatures. In this investigation, loss in sample weight was recorded electronically⁴ as a function of temperature and time, while furnace temperature was continuously increased at a rate of 5°C. per minute from room temperature to 600°C. The kinetics of reaction were evaluated from the resulting curves by the method of Freeman and Carroll.⁵ This technique permits one to investigate systems over an entire temperature range of reaction continuously as well as to observe transitions from one reaction mechanism to another with the use of a single experimental curve. Differential thermal analysis complemented the thermogravimetric phase of the work in elucidating the mechanism of degradation. Experiments were run in argon to clarify certain aspects of the mechanism of degradation in air. The ingredients and products of decomposition composing the polymer were determined by mass spectrometry and infrared analysis.

EXPERIMENTAL

A. Material

Laminac 4116 was purchased from the American Cyanamid Company in the form of a viscous solution consisting of an unsaturated polyester and 30 per cent styrene monomer. The polymer was prepared by a condensation reaction involving a glycol and two dicarboxylic acids, one of which was unsaturated. A crosslinking reaction of the

styrene, used as both a solvent and copolymer, was effected by the addition of initiators, 1.5 per cent of Lupersol and 0.5 per cent Nuodex, to form a solid network structure. From infrared analysis of the polymer and possible ingredients it was determined that the polymer consisted of phthalic and maleic anhydrides and propylene glycol. The composition of polyesters of this type is commonly 20% for each of the acids and 40% for the glycol. The molecular weight of the polymer could not be determined, since it cannot be dissolved or liquefied without decomposition. The carbon, hydrogen, and oxygen contents were found to be 72, 6, and 22 per cent, respectively.

B. Apparatus and Procedure

Changes in sample weight were followed by means of a Chevenard thermobalance which was modified for electronic recording.⁴ Two hundred-milligram samples were placed in #000 Coors glazed porcelain crucibles and heated at a rate of 5°/min. from ambient temperature to approximately 600°C. Temperature measurements were made with a B&S No. 28 Gage chromel-alumel thermocouple located 1/4 in. above the crucible and 1/4 in. from the furnace wall. Experiments were carried out both in air and while passing argon over the sample to maintain an inert atmosphere. Moseley, Model 3, X-Y recorders were used with the thermobalance to automatically record changes in weight as a function of temperature and for obtaining differential thermal analysis curves.

The rates of weight loss were calculated from tangents to the thermogravimetric curves. A plot of the derivative of loss in weight with respect to time vs. temperature shows several overlapping reaction bands (Fig. 4). In order to evaluate the chemical kinetics associated with a specific band,

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it is necessary to determine the area related to the band. A correction in area should be made where overlap resulting from interfering reactions contributes significantly to the area. For this purpose the band is extrapolated linearly to the abscissa as illustrated in Figure 1. A line was then drawn from the point of intersection of the two bands C, to the midpoint between them on the abscissa at D. The corrected area of the ACF band was taken as the total area under the curve minus the area of the triangle, CDF, on the side of the interfering reaction band ECB. This procedure was applied only to the first stage of degradation in air. Due to the extensiveness of interference, the second and third stages in air as well as the two in argon were treated as one stage in each of the gaseous environments. In these zones, rates were taken over the temperature interval 300 to 340°C. in air and from 210 to 330°C. in argon.

The differential thermal analysis apparatus⁶ consisted of series connected chromel-alumel thermocouples, one placed in 2 g. of sample and the other in an equivalent volume of inert reference material, powdered alumina. The difference in temperature between the sample and thermally inert material, both of which are heated simultaneously, is recorded continuously as a function of time and sample temperature. A two-hole nichrome block located in the furnace contained two pyrex test tubes into which the sample and reference materials were placed. These tubes⁷ were cut down so that their tops extended no more than 1/4 in. above the furnace block. The thermocouples were inserted into pyrex thermocouple wells which were fused to the upper portion of the tube and centered 0.5

cm. from the bottom. These tubes prevented movement of the thermocouple during melting and boiling and eliminated refluxing which may have resulted in reaction between condensate and reactant. The argon atmosphere was maintained by passing the gas over both the sample and reference material. A Model JPG Gardsman indicating pyrometric stepless program controller purchased from the West Instrument Co. was used to monitor the heating rate, 15°C. per minute.

The products of thermal degradation in air were determined by heating a 3.0 gram sample of Laminac at a rate of 5°C. per minute in a stream of air. The products were swept into a train of six series-connected vessels. The first two were maintained at 0°C. by ice baths and the remaining pairs contained water and ethanol, respectively, at room temperature. Three such trains were connected in succession to collect reaction products evolved over the three temperature ranges of ambient to 300°C., 300 to 400°C., and 400 to 500°C. The products were identified by infrared analysis with the use of the Perkin-Elmer double-beam recording infrared Spectrophotometer Model No. 21 and by standard chemical procedures.

The course of decomposition in air was also followed by measuring changes in volume due to the formation of gaseous products as the temperature of a 1.0-g. sample was increased at a rate of 10°C. per minute from room temperature to 600°C. The buret used automatically maintained the system at constant pressure.⁸ A Dry Ice-acetone bath was located between the reaction vessel and

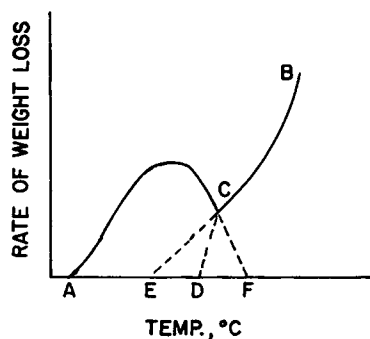


Fig. 1. Resolution of reaction areas: (C) point of intersection of band AC with band CB; (CE) linear extension of band CB to base line; (CF) linear extension of band AC to base line; (D) midpoint of EF.

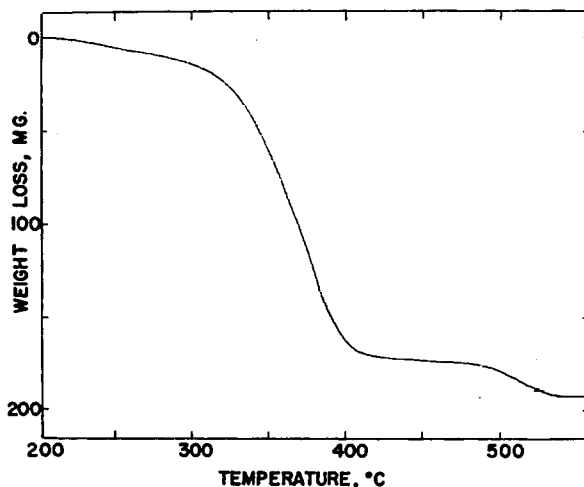


Fig. 2. Thermogravimetric curve of 200 mg. Laminac 4116 in air; heating rate, 5°C./minute.

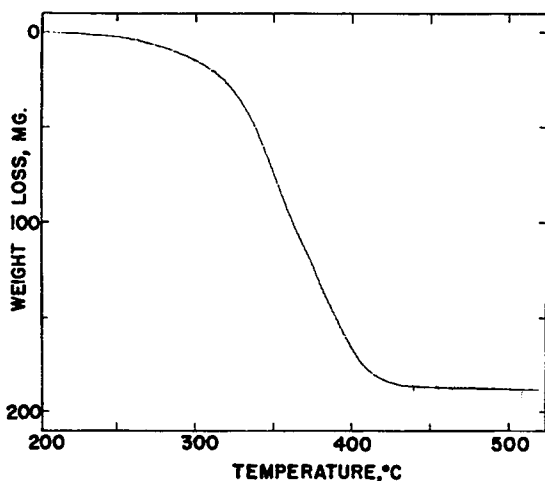


Fig. 3. Thermogravimetric curve for the degradation of Laminac 4116 in argon at atmospheric pressure; 200 mg. sample heated at 5°C./minute.

gas buret. The gases in the buret were transferred to a gas collecting bulb and analyzed with the G.E. analytical model mass spectrometer.

RESULTS

Figure 2 is a graph of weight loss as a function of temperature for the thermal degradation of 200 mg. of the polyester, Laminac 4116, in air from 200 to 550°C. Decomposition began at approximately 200°C., and was relatively rapid from 300 to 418°C. Up to this point, there was an 87% loss in sample weight. From 418 to 490°C., little change occurred. At 490°C. the reaction became relatively rapid and was complete at 550°C. The total weight loss corresponded to 97% of the initial weight of the reactant.

The thermogravimetric curve for decomposition of the polymer in argon from 200 to 500°C. at atmospheric pressure is shown in Figure 3. As in air, degradation commenced at 200°C.; however, the reaction was complete at 450°C., leaving 6% residue. It may be noted that the last stage of reaction observed in air from 450° to 550°C. did not occur in argon.

Figure 4 shows graphs of rate of change in weight as a function of temperature in air and argon, respectively. In air, four stages of reaction are evident, as indicated by the band structure of the curve. The first occurs over the temperature interval of 200 to 260°C.; the second, third, and fourth stages occur over the temperature ranges of 260 to 360°C., 360 to 450°C., and 450 to 550°C., respectively. The maximum rates of change in

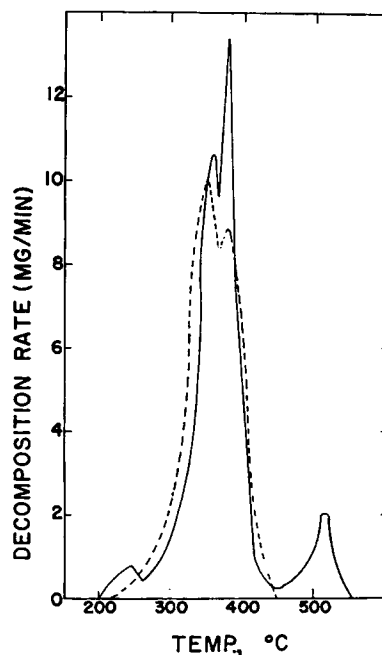


Fig. 4. Derivative thermogravimetric curves for the thermal degradation of Laminac 4116: (—) in air; (---) in argon.

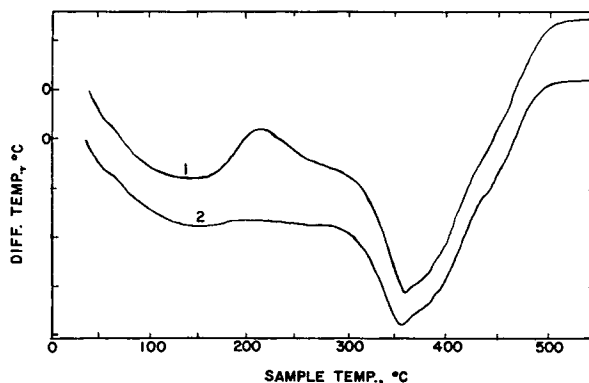


Fig. 5. Differential thermal analysis curves for 2-g. samples of Laminac 4116 in (1) air and (2) argon; heating rate, 10°C./minute; upward direction is exothermal, downward direction, endothermal. Each division on differential temperature scale, 10°C.

sample weight which correspond to each of these bands are 2, 27, 34, and 5 mg. per minute, respectively. Overlap between reactions is apparent in Figure 4, the most extensive being the transition from the second to third stage of degradation. Overlap between the first and second and between the third and fourth regions is relatively small, the former being more appreciable than the latter.

In argon, degradation takes place in two stages with extensive overlap, the first over the temperature

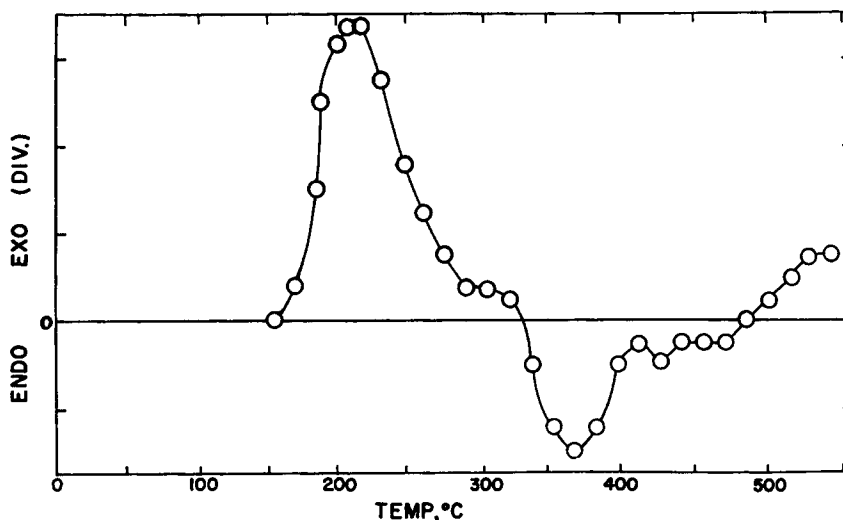


Fig. 6. Difference in differential temperature between Laminac 4116 heated in air and argon as a function of sample temperature. Upward direction is exothermal, downward direction endothermal; 2.5°C. per division.

interval of 200 to 365°C. and the second from 365 to 450°C. The maximum rates of weight loss are 25 and 23 mg. per minute, respectively.

Figure 5 shows two differential thermal analysis curves, one for the polyester in air and the second in argon. In both cases an endothermal trend is observed up to approximately 100°C. Between 160 and 290°C. an exotherm occurs in air, which is absent in argon, with a peak at 213°C. From 290 to 490°C., both curves exhibit endotherms, the minima being at approximately 365°C. Copious quantities of white and yellow vapors were observed during reaction in this region.

A comparison between the thermal degradation of the polyester in air and argon is shown in Figure 6, which is a difference plot of the differential thermal analysis curves in Figure 5. The curve in argon is subtracted from that in air. Two regions of relative exothermicity are apparent, one from 150 to 290°C., and the other from 470 to 550°C. The former is considerably more exothermal than the latter. It is also evident from this figure that degradation in air over the temperature range of 290 to 413°C. is more endothermal than decomposition in argon.

To further investigate the nature of the exothermal reaction in air, 0.5 g. of the polymer was heated in oxygen at 160°C. After 18 hours, the sample lost 2% of its original weight. Infrared analysis did not detect chemical changes.

A three-gram sample was heated at a rate of 5°C. per minute in a stream of air from room temperature to 500°C. and the products of reaction collected in a series of vessels as described

in the experimental section. The substances identified in the first two receivers maintained at 0°C. were: benzaldehyde (I) and unsaturated hydroxy esters (II) over the temperature range of 200 to 300°C.; phthalic anhydride (III) and a dark yellow, oily liquid containing hydroxy esters from 300 to 400°C.; a mixture of phthalic acid and phthalic anhydride in addition to a yellow liquid containing low molecular weight esters of propylene glycol from 400 to 500°C.

The change in volume due to the formation of gaseous products accompanying the thermal decomposition in air of one gram of the polyester was measured as a function of temperature and time from room temperature to 550°C. at constant pressure. Since a Dry Ice-acetone trap was interposed between the reaction vessel and gas buret, only the volume of noncondensables was measured and collected. Increases in volume were first observed at approximately 260°C. The principal gases formed were: carbon dioxide (IV), 67.0%; hydrogen, 19.9%; methane 7.4%; and propylene (V), 3.4%. The total volume of gas was 40 ml.

The kinetics of reaction in air and argon were evaluated from the derivative thermogravimetric and thermogravimetric curves shown in Figures 1, 2, 3, and 4 by the method of Freeman and Carroll.⁵ The equation used was:

$$\frac{\Delta \log (dw/dt)}{\Delta \log W_r} = x - \frac{E^*}{2.3R} \frac{\Delta \frac{1}{T}}{\Delta \log W_r} \quad (1)$$

where:

- dw/dt = rate of change in weight
 W_r = weight of reactant at any time
 E^* = energy of activation
 R = gas constant
 T = absolute temperature
 x = order of reaction

Figure 7 is a graph of $(\Delta \log dw/dt)/\Delta \log W_r$ vs. $(\Delta T^{-1})/\Delta \log W_r$ for the degradation of the polyester in air. Three linear relationships were obtained. These represent (a) the first stage of reaction, (b) the combined second and third stages of degradation, and (c) the fourth and last stage

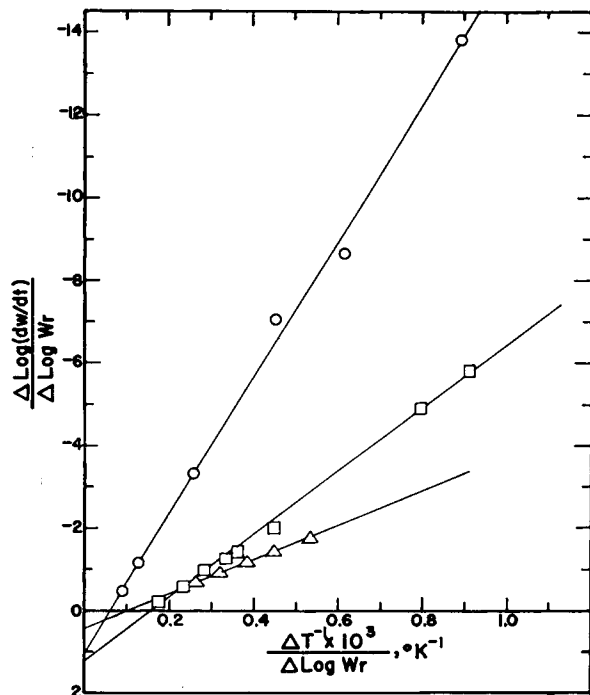


Fig. 7. Kinetics of the thermal degradation of Laminac 4116 in air.

(Δ) Initial stage of reaction. (□) Second and third stages of reaction. (○) Fourth stage of reaction.

of reaction. The corresponding orders of reaction and energies of activation, given in Table I, were determined from the intercepts and slopes of the lines and are: 0.4, 1.2, and 1.0, respectively, and 19, 35, and 79 kcal. mole⁻¹, respectively. The first order frequency factors, A , were calculated from the expression

$$\ln \frac{dw/dt}{W_r} = \ln A - \frac{E^*}{RT} \quad (2)$$

The values are: 1.3×10^5 , 2.7×10^9 , and 4.2×10^{19} sec.⁻¹, respectively.

Figure 8 is a similar graph for the reaction in argon. The linear relationship obtained represents the combined first and second stages of degradation. From the intercept and slope of this line the order

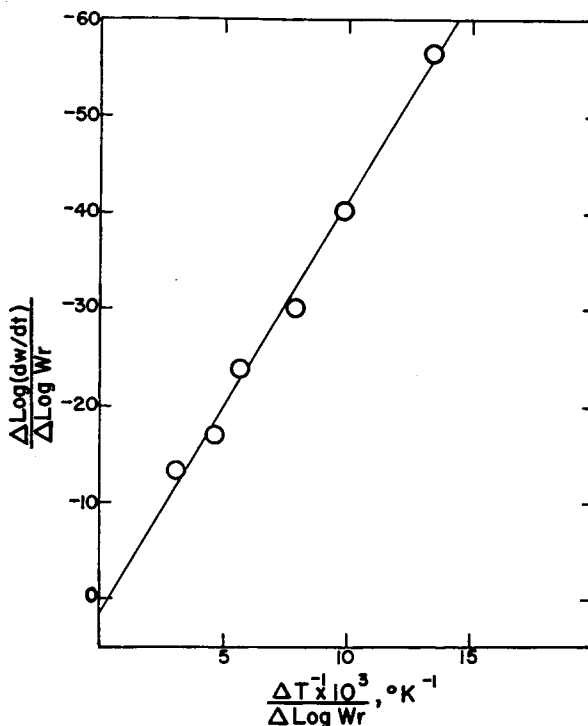
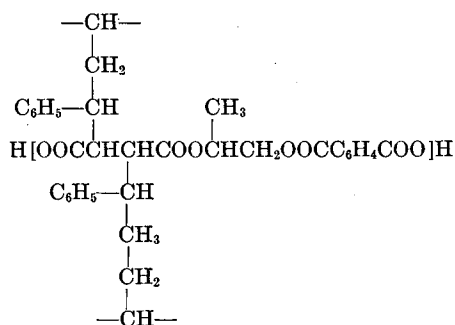


Fig. 8. Kinetics of the thermal degradation of Laminac 4116 in argon.

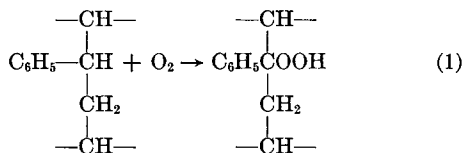
of reaction was found to be unity and the energy of activation 20 kcal./mole⁻¹. The first-order frequency factor is 4.8×10^3 sec.⁻¹.

DISCUSSION

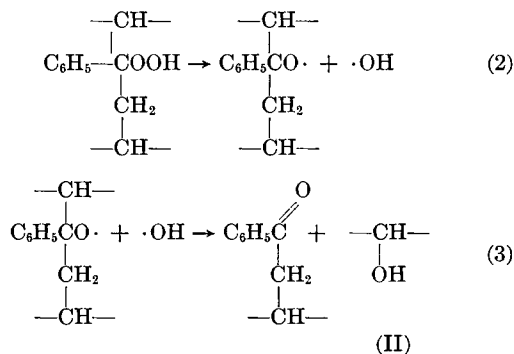
The mechanism of degradation of the polyester in air differs from that in argon. This is apparent from Figure 4, which shows four zones of reaction in air and two in argon, respectively. During the initial stage of degradation in air, the weight loss is associated with an exothermal reaction. This is not the case in argon. The formation of an unstable hydroperoxide intermediate would appear to account for these results as well as for the formation of benzaldehyde and hydroxyesters as products of degradation in air. The reaction probably involves attack by oxygen at the alpha carbon of the styrene constituent of the polymer, which is followed by rearrangement. Based on infrared analysis the unit basic structure of the polyester is taken to be



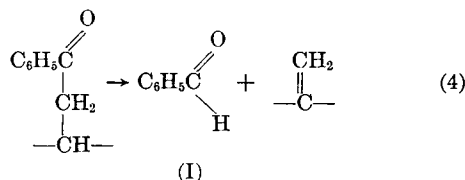
The mechanism of thermal degradation indicated from the products and energetics of reaction appears to involve hydroperoxidation at the alpha carbon of the styrenated branch of the polymer. This would account for the exotherm observed during this phase of reaction.



Rearrangement follows:



Cleavage may occur between the carbonyl carbon and α carbon, followed by hydrogen transfer from the β carbon to the benzoyl radical.



The energy of activation was determined to be 19 kcal. per mole. This is in the range of values reported for hydroperoxide formation which vary from 15 to 35 kcal. per mole, depending on the ease of penetration of oxygen into the polymer lattice.⁹

Vaporization as the rate-controlling mechanism for the thermal degradation of the polyester in ar-

TABLE I
Kinetic Parameters for Thermal Degradation
of Laminac 4116

Stage of reaction	Temp. range, °C.	Order of reaction	Energy of activation, kcal. mole ⁻¹	First order frequency factor, sec. ⁻¹
a. In air				
1	200-260	0.4	19	1.3 × 10 ⁵
2, 3	260-450	1.2	35	2.7 × 10 ⁹
4	450-550	1.0	79	4.2 × 10 ¹⁹
b. In Argon				
1, 2	200-450	1.0	20	4.8 × 10 ³

gon does not appear likely, since the order of reaction is unity and the energy of activation, 20 kcal. per mole, appears to be too low for high molecular weight, crosslinked, polyester-type polymers. The low energy of activation may be accounted for by a rate-controlling mechanism involving diffusion of unreacted molecules to the surface where decomposition occurs. Preferential decomposition at the surface appears reasonable, since both the free energy and temperature of molecules at the surface should be relatively high with respect to the interior.

At 260 and 370°C., the mechanism of reaction in air changes, as is indicated by the beginning of the second and third bands in the derivative thermogram. This is also evident from differential thermal analysis, where the exotherm representing the initial reaction zone is complete and an endothermal region begins. The extent of weight loss and rate of weight loss in the second and third reaction zones are approximately ten times that of the first.

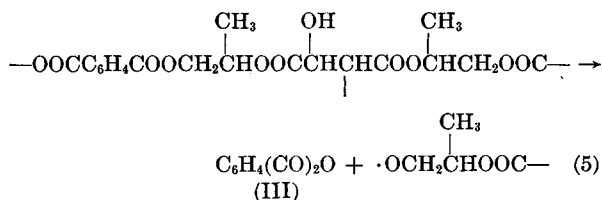
Since the second and third zones of reaction are endothermal, bond rupture is indicated in these regions. The species involved, principally products formed during the first stage of reaction in air, are apparently not the same molecules undergoing decomposition in the two stages of reaction in argon. This is indicated by (1) the difference in the extent of weight loss which was 7% greater after the third stage in air than after the second in argon, (2) the greater endothermicity of the reaction in air, as well as (3) differences in the energies of activation and frequency factors, 35 kcal. per mole and 2.7 × 10⁹ per sec., and 20 kcal. per mole and 4.8 × 10³ per sec., in air and argon, respectively.

When the polyester was heated in the volumetric

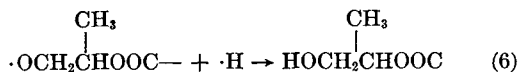
apparatus in which a Dry Ice-acetone trap was interposed between the reaction vessel and the gas buret, increases in volume where first observed at approximately the second stage of degradation in air. This indicates that the reaction products formed during the initial stage of degradation were condensed, and that the noncondensable gaseous products are formed in the second and third reaction zones. These gases were determined to be hydrogen, carbon dioxide, methane, and propylene. The relatively high percentage of CO₂ indicated extensive decarboxylation of the polyester.

The energy of activation, order of reaction, and frequency factor given in Table I for the combined second and third stages of degradation in air are of the order expected for the rupture of chemical bonds.^{3,10} In accordance with the products of reaction, the following free radical mechanism is suggested.

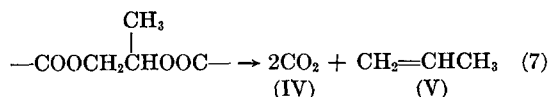
Cleavage occurs at the carboxyl oxygen to form phthalic anhydride:



The hydroxy ester may then be formed by reaction with hydrogen:



Decarboxylation of the polyester should occur readily and account for the formation of propylene and CO₂



As higher temperatures are attained, lower molecular weight fragments are formed, leaving a carbonaceous residue.

Over the temperature interval 450 to 550°C., the derivative thermogram, Figure 4, shows a fourth reaction zone in air which is absent in argon. The difference differential thermal analysis curve, Figure 7, displays an exothermal trend in this temperature region. These results appear to indicate oxidation of the carbon formed during the third stage of reaction. This was further confirmed

from the kinetics of reaction which were found to be first order with an overall energy of activation of 79 kcal. mol. These values are in agreement with the reported values for the reaction between carbon and oxygen which are unity¹¹ and 80 kcal./mole,¹² respectively. A residue of carbon was found after decomposition was complete in argon.

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Synopsis

The kinetics of the thermal decomposition of the polyester, Laminac 4116, were investigated in air and argon at atmospheric pressure by means of a continuous recording thermobalance and by differential thermal analysis. Samples were heated from ambient temperature to 600°C. at rates of 5°/min. and 15°/min. In air and argon, decomposition commences at 200°C. and is complete at 550 and 450°C., respectively. Four modes of degradation in oxygen and two in argon are indicated from derivative plots of the thermogravimetric curves. The kinetics of reaction were evaluated by the method of Freeman and Carroll. In the presence of air, the initial stage of reaction appears to involve formation of an unstable hydroperoxide intermediate which undergoes rearrangement and degradation. The energy of activation was calculated to be 19 kcal./mole. An exotherm corresponding to this first stage of degradation is observed by differential thermal analysis. The second and third stages of reaction in air correspond approximately to the two stages in argon with respect to their endothermal nature and to the temperature regions over which they occur. Mass spectrometric and infrared analyses were employed for identification of gaseous and volatile products. The fourth stage of reac-

tion in air appears to involve the oxidation of carbon to carbon dioxide. Mechanisms of reaction are proposed and discussed.

Résumé

La cinétique de la décomposition thermique du polyester, Laminac 4116, a été étudiée sous air et sous argon à pression atmosphérique au moyen d'une thermobalance à enregistrement continu et par analyse thermique différentielle. Les échantillons ont été chauffés jusqu'à 600°C en partant de la température ambiante à des vitesses allant de 5 à 15°/min. Sous air et sous argon la décomposition débute à 200°C et est complète à 550° et 450°C respectivement. Quatre types de dégradation sous oxygène et deux sous argon sont indiqués par les diagrammes dérivés des courbes thermogravimétriques. La cinétique de la réaction a été interprétée par la méthode de Freeman et Carroll. En présence d'air l'étape initiale de la réaction semble faire intervenir la formation d'un hydroperoxyde intermédiaire instable qui subit un réarrangement et une dégradation. L'énergie d'activation s'élève à 19 Kcal/mole. Une réaction exothermique correspondant à cette première étape de la dégradation est observée par analyse thermique différentielle. Les seconde et troisième étapes de la réaction sous air correspondent approximativement aux deux étapes sous argon pour ce qui concerne leur nature endothermique et les domaines de température où elles s'effectuent. Des analyses au spectromètre de masse et des analyses infrarouge ont été employées pour identifier les produits gazeux et volatils. La quatrième étape de la réaction dans l'air semble faire intervenir l'oxydation du carbone en anhydride carbonique. Des mécanismes de réaction sont proposés et discutés.

Zusammenfassung

Die Kinetik der thermischen Zersetzung des Polyesters Laminac 4116 wurde unter Luft und unter Argon bei Atmosphärendruck mittels einer kontinuierlich anzeigenden Thermowage und durch thermische Differentialanalyse untersucht. Die Proben wurden von Raumtemperatur auf 600°C mit Geschwindigkeiten von 5 und 15°/min erhitzt. Unter Luft und unter Argon beginnt die Zersetzung bei 200°C und ist bei 550 bzw. 450°C vollständig. Differentialdiagramme der thermogravimetrischen Kurven lassen vier Abbauvorgänge in Sauerstoff und zwei in Argon erkennen. Die Kinetik der Reaktion wurde nach der Methode von Freeman und Carroll ermittelt. In Gegenwart von Luft scheint im Anfangsstadium der Reaktion ein instabiles Hydroperoxyd als Zwischenprodukt aufzutreten, das eine Umlagerung erfährt und abgebaut wird. Die Aktivierungsenergie wurde zu 19 kcal/Mol berechnet. Ein exothermer Vorgang, der diesem Anfangsstadium des Abbaus entspricht, wird bei der thermischen Differentialanalyse beobachtet. Die zweite und dritte Phase der Reaktion unter Luft entsprechen in bezug auf ihren endothermen Charakter und auf das Temperaturbereich, in dem sie ablaufen, angenähert den beiden Phasen des Prozesses unter Argon. Zur Identifizierung der gasförmigen und flüchtigen Produkte wurden Massenspektroskopie und Infrarotanalyse angewendet. Die vierte Phase der Reaktion in Luft scheint in der Oxydation von Kohlenstoff zu Kohlendioxyd zu bestehen. Reaktionsmechanismen werden vorgeschlagen und diskutiert.

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