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THERMAL DECOMPOSITION PRODUCTS OF POLY (VINYL ALCOHOL)

BY

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DECOMPOSITION THERMIQUE DES PRODUITS D'ALCOOL POLYVINYLIQUE

SOMMAIRE

La décomposition thermique d'alcool polyvinylique se fait en deux étapes. Dans une étude de la première étape de décomposition, la pyrolise du polymère a été faite dans le vide à 240°C durant quatre heures et les produits ont été déterminés à l'aide de chromatographie en phase gazeuse. Les principaux dérivés sont de l'eau, des aldéhydes ayant comme formule générale $HC(=O){-}(CH=CH)_n{-}CH_3$ et des cétones de méthyl ayant comme formule $H_3C-C(=O){-}(CH=CH)_n\ CH_3$, alors que n = 0, 1, 2, 3, etc. Les mécanismes pour la formation de ces composés carbonyles sont étudiés.

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Thermal Decomposition Products of Poly(vinyl Alcohol)

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Synopsis

The thermal decomposition of poly(vinyl alcohol) is known to occur in two stages. In a study of first-stage decomposition, this polymer was pyrolyzed in vacuum at 240°C for 4 hr and the products were determined by using gas chromatography. The main products were water, aldehydes having the general formula $HC(=O)\text{-}(CH{=}CH)_n\text{-}CH_3$, and methyl ketones having the formula $H_3C\text{—}C(=O)\text{-}(CH{=}CH)_n\text{-}CH_3$, where $n = 0, 1, 2, 3$, etc. Mechanisms for the formation of these carbonyl compounds are discussed.

INTRODUCTION

The thermal decomposition of poly(vinyl alcohol) occurs in two stages.[1] The first stage, which begins at about 200°C, is mainly dehydration, accompanied by the formation of some volatile products; the residue is predominantly macromolecules having polyene structure. The published data on the volatile thermal decomposition products of this polymer are not only very limited, but are also conflicting. Yamaguchi and Amagasa[2] analyzed the products of the first-stage decomposition by chemical methods and found acetaldehyde, crotonaldehyde, benzaldehyde, and acetophenone. Kaesche-Krischer and Heinrich[3] found formaldehyde, acetaldehyde, and acrolein. Ettre and Varadi[4] used a pyrolysis–gas chromatographic technique and reported that the main organic products formed at a pyrolysis temperature of 500°C were acetaldehyde and acetic acid. They also found smaller amounts of ethanol, methyl acetate, and some hydrocarbons. At this temperature both stages of decomposition must have occurred. In second-stage decomposition of poly(vinyl alcohol), the macromolecules having polyene structure are degraded to produce carbon and hydrocarbons. Gilbert and Kipling[5] analyzed the gases formed in the second-stage decomposition of vinyl polymers.

The authors of this paper are primarily interested in first-stage decomposition. The only important agreement in the data presented by others[2–4] was the finding that acetaldehyde is one of the major products. The purpose of the present investigation is to obtain more reliable information about the thermal decomposition products of poly(vinyl alcohol) by using the latest techniques in gas chromatography. The experimental data will be used to discuss the mechanism of thermal decomposition of poly(vinyl alcohol).

EXPERIMENTAL

Material

A commercial grade of poly(vinyl alcohol) (>99% hydrolysis) was dried at 80°C under vacuum for 48 hr, prior to pyrolysis. The molecular weight of the polymer was found to be about 130000 by a viscosity method.

Thermal Decomposition

The apparatus for the thermal decomposition of poly(vinyl alcohol) was similar to that used for a previous study.[6] A sample weighing 1 g was placed in a Pyrex tube connected to a liquid nitrogen trap and a vacuum pump. After the system was evacuated to 1×10^{-4} mm Hg, the vacuum line to the pump was closed and the sample was heated at 240°C for 4 hr. Most of the volatile decomposition products were collected in a liquid nitrogen trap. When the liquid nitrogen was removed, the condensates in the trap separated into two layers: a water layer and an oil layer. The fraction volatile at room temperature was transferred from the trap into a gas sampling bottle of known volume. The three fractions were analyzed separately, and the combined amounts of each component were obtained.

The pyrolysis tube containing the solid residue was evacuated again, and the residue pyrolyzed at 450°C for 4 hr. The products from the second-stage decomposition were analyzed in the same way as those from the first-stage decomposition.

Analysis

The chromatographic conditions that were used to analyze the decomposition products are presented in Table I. The identification of the peaks was carried out as follows: (*a*) comparison of retention times with those of known compounds by use of three different columns; (*b*) collection of products that yield certain peaks by preparative gas chromatography, followed by chemical methods of identification; (*c*) determination of carbon structure of products by catalytic hydrogenation.[7] For quantitative analysis, the areas under each peak were measured, and approximate substance correction factors were applied.[8]

RESULTS AND DISCUSSION

The results of the products from the first-stage decomposition of poly(vinyl alcohol) are presented in Figure 1. The quantitative data are represented by line charts, plotted against the retention indices. The reten-

TABLE I
Gas Chromatographic Conditions

No.	Type of column	Stationary phase	Carrier gas Type	Carrier gas Pressure, psi	Detector	Temperature	Purpose
1	Support coated open tubular, 100 ft, 0.02 in. ID	Carbowax 20 M	Helium	5	Flame ionization	Isothermal at several temperatures between 60 and 240°C	Identification of components; quantitative analysis
2	Open tubular, 150 ft, 0.01 in. ID	Didecyl phthalate	Helium	10	Flame ionization	Isothermal at several temperatures between 25 and 150°C	Identification of components
3	Packed 2 m, $^1/_4$ in. OD	Tetraethylene glycol dimethyl ether (Perkin-Elmer column F)	Helium	20	Thermal conductivity	25, 80°C	Identification of oxygenated compounds
4	Support coated open tubular, 100 ft, 0.02 in. ID	Squalane	Helium	5	Flame ionization	0, 50, 100°C	Identification of hydrocarbons
5	Packed, 6 ft, $^1/_8$ in. OD	60–80 mesh silica gel deactivated with 4% silicone oil DC 200	Helium	20	Flame ionization	Programmed 10°C/min from 60 to 200°C	Identification of C_1–C_4 hydrocarbons
6	Preparative, 10 ft, $^3/_8$ in. OD	8% Carbowax 1540 on 60–80 mesh Chromosorb P	Helium	20	Thermal conductivity	80, 120°C	Trapping major peaks
7	Catalytic hydrogenation tube (1% Pd on Chromosorb) $^1/_4$ in. O.D. in series with support coated (squalane) open tubular, 100 ft, 0.02 in. ID		Hydrogen	10	Flame ionization	Catalytic tube: 250°C Squalane: 0 and 50°C	Determination of chemical structure

tion index of each component was determined by using n-alkanes as standards at gas chromatographic condition 1.

The major peaks, A_0, A_1, A_2, and A_3 of Figure 1, are spaced uniformly on the retention index scale, suggesting that they belong to the same homologous series. The first three were identified as acetaldehyde, crotonaldehyde, and 2,4-hexadiene-1-al by comparing their retention indices with

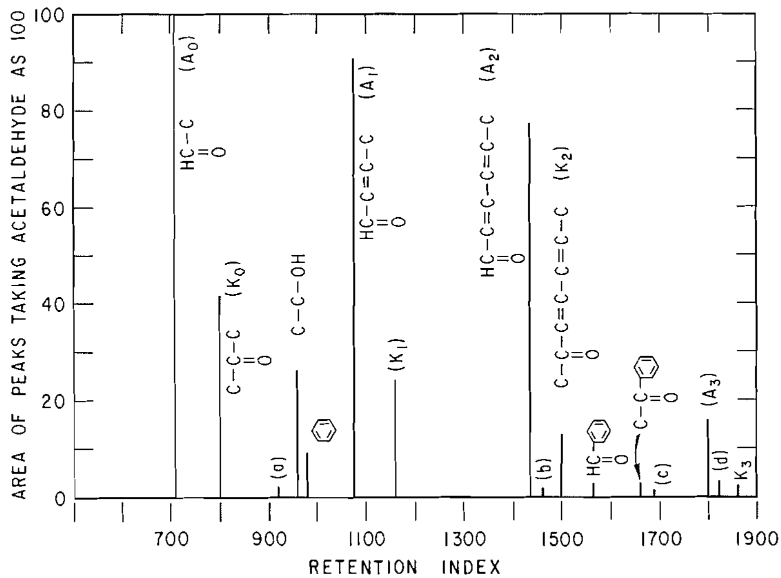


Fig. 1. First-stage decomposition products of poly(vinyl alcohol). Area of peaks vs. retention index.

those of known compounds and by the determination of melting points of 2,4-dinitrophenylhydrazones of the three products. The general formula of these compounds is I:

$$\underset{\displaystyle \text{O}}{\overset{}{\text{HC}}}\!\!\!\overset{}{\|}\!\!\left(\text{CH}{=}\text{CH}\right)_n\text{CH}_3 \qquad n = 0, 1, 2$$

I

Peak A_3 is believed to be due to 2,4,6-octatriene-1-al, the next compound in the same series. This suggestion is supported by the fact that n-heptane was obtained on catalytic hydrogenation of this product.

Peaks K_0, K_1, K_2, and K_3 are also uniformly spaced and thus appear to be due to another homologous series. The first peak, K_0, was due to acetone. The second peak, K_1, which yielded a positive iodoform test and produced pentane by catalytic hydrogenation, was believed to be due to 3-pentene-2-one. Although 2-pentanol and 2-pentanone should yield the same results on these two tests, their retention indices are different. The third peak, K_2, was identified as 3,5-heptadiene-2-one by comparing the retention time with that from a synthesized sample.[9] The general formula for this homologous series is II:

$$CH_3-\underset{\underset{O}{\|}}{C}-(CH=CH)_n-CH_3$$

II

TABLE II
Thermal Decomposition Products of Poly(vinyl Alcohol)
(240°C, 4 hr)

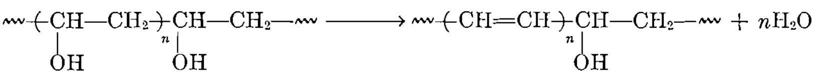
Product	Wt.-% of original polymer
Water	33.4
Carbon monoxide	0.12
Carbon dioxide	0.18
Hydrocarbons C_1–C_3	0.01
Acetaldehyde	1.17
Acetone	0.38
Peak a	0.025
Ethanol	0.29
Benzene	0.06
Crotonaldehyde	0.76
K_1 (3-pentene-2-one)	0.19
2,4-hexadiene-1-al	0.55
Peak b	0.014
3,5-Heptadiene-2-one	0.099
Benzaldehyde	0.022
Acetophenone	0.021
Peak c	0.017
A_3 (2,4,6-octatriene-1-al)	0.11
Peak d	0.026
K_3 (3,5,7-nonatriene-2-one)	0.020

TABLE III
Decomposition Products of Poly(vinyl Alcohol)
(Material Balance, in Weight Percentage of Original Polymer)

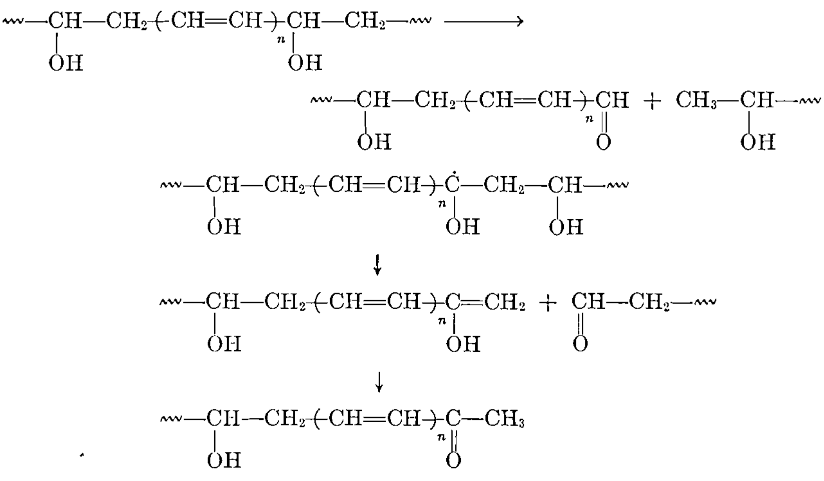
1st stage (240°C, 4 hr)				2nd stage (450°C, 4 hr)		
Volatiles 47.9	Water layer	Water	33.4	Volatiles 27.7	Water layer	0.60
		Org. Compds.	1.56			
	Oil layer	Org. Compds. Analyzed	1.19		Oil layer	22.30
		Not analyzed	4.99			
	Gas	0.92			Gas	2.46
	Loss	5.81			Loss	2.34
Residue 52.1				Residue 24.4		

The decomposition products reported by others[2-4] but not found in the present investigation were formaldehyde, acrolein, methyl acetate, and acetic acid. The difference in polymer samples could account for the discrepancy in the production of acetic acid, because poly(vinyl alcohol) samples are known to contain different amounts of acetyl groups.

The experimental data on the thermal decomposition products of poly(vinyl alcohol) are presented in Table II, and the data on material balance in Table III. The main decomposition products of the first stage were water and carbonyl compounds. The distribution of oxygen compounds in the products, based on 100 monomer units in the original polymer, was: water, 86.4 mole; aldehydes, 1.9 mole; ketones, 0.5 mole; other, 0.7 mole. Water is formed by a mechanism similar to that forming hydrogen chloride from poly(vinyl chloride) and acetic acid from poly(vinyl acetate), leaving a residue having conjugated polyene structure [eq (1)].


(1)

Scission of some of the C-C bonds results in the formation of the carbonyl ends. Aldehyde and methyl ketone end formation are expected to proceed as shown in eqs. (2) and (3), respectively.

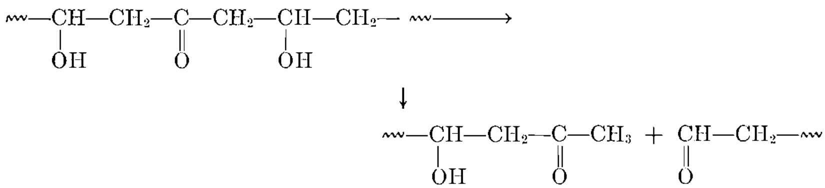

(2)

(3)

The formation of acetaldehyde, crotonaldehyde, 2,4-hexadiene-1-al, and 2,4,6-octatriene-1-al is plausible from the aldehyde ends, and the formation of acetone, 3-pentene-2-one, and 3,5-heptadiene-2-one is expected from the methyl ketone ends.

Considerably more aldehydes than ketones were found in the products. This difference was predictable from these reactions, because the aldehyde ends can be formed by both reactions (2) and (3), whereas the ketone ends are formed by the latter reaction only.

Yamaguchi and Amagasa[10] predicted the formation of the series of aldehydes and ketones (found in the present study) from the mechanisms of decomposition that they proposed. They suggested that the methyl ketone ends are formed from the carbonyl groups that are present in the original polymer [eq (4)].



(4)

The present authors suggest that the transfer of a hydrogen atom from a tertiary carbon followed by a decomposition reaction (3) could also account for the formation of methyl ketone ends.

A large portion of the oil layer was not analyzed (as noted in Table III), because most of these products were not sufficiently volatile for the gas chromatographic conditions used. The conversion of the carbonyl compounds in the oil layer to 2,4-dinitrophenylhydrazones resulted in a large yield, indicating that the carbonyl compounds represented a large portion of this layer.

The volatile decomposition products of the second stage were mainly hydrocarbons; series of *n*-alkanes, *n*-alkenes, and aromatic hydrocarbons were found. The second-stage pyrolysis products of poly(vinyl chloride) and poly(vinyl acetate) were also determined for comparison with those from poly(vinyl alcohol). The similarity in both the qualitative and quantitative data of the products from the three polymers indicates that the same mechanism applies to the second-stage decomposition of each of the three vinyl polymers.

CONCLUSION

Analysis by gas chromatography showed that the first-stage thermal decomposition products of poly(vinyl alcohol) are mainly composed of water, aldehydes having the general formula $\underset{\underset{O}{\|}}{CH}\text{—}(CH{=}CH)_n\text{—}CH_3$ and methyl ketones having the formula $CH_3\text{—}\underset{\underset{O}{\|}}{C}\text{—}(CH{=}CH)_n\text{—}CH_3$, where n = 0, 1, 2, 3, etc. According to the mechanisms proposed in this study, dehydration is accompanied by some scission of the polymer chain, resulting in the formation of aldehyde ends by one type of reaction and of both aldehyde and methyl ketone ends by another type. These mechanisms explain the formation of these carbonyl compounds.

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