JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 1887–1899 (1970)

High-Temperature Pyrolysis of Poly(vinyl chloride): Gas Chromatographic-Mass Spectrometric Analysis of the Pyrolysis Products from PVC Resin and Plastisols

MICHAEL M. O'MARA, *B. F. Goodrich Chemical Company, Avon Lake, Ohio 44012*

Synopsis

A pyrolysis gas chromatographic mass spectrometric technique for analyzing the pyrolysis products from polymers in an inert atmosphere is described. Initial studies encompassing the pyrolysis of poly(vinyl chloride) homopolymer and a series of PVC plastisols (based on *o*-phthalate esters) have provided a complete qualitative and semiquantitative analysis of the pyrolysis products from these materials. PVC resin yields a series of aliphatic and aromatic hydrocarbons when pyrolyzed at 600°C; the amount of aromatic products is greater than the amount of aliphatic products. Benzene is the major organic degradation product. A typical PVC plastisol [PVC/*o*-dioctyl phthalate (100/60)] yields, upon pyrolysis, products that are characteristic of both the PVC matrix and the phthalate plasticizer. The pyrolysis products from the plasticizer dilute those from the PVC portion of the plastisol and are, in turn, the major degradation products. There are no degradation products resulting from an interaction of the PVC with the plastisol. The pyrograms resulting from pyrolysis of the various plastisols of PVC can be used for purposes of "fingerprinting." Identification of the major peaks in a typical plastisol pyrogram provides information leading to a precise identification of the plasticizer. The pyrolysis data from this study were related to a special case of flammability and toxicity.

INTRODUCTION

The mechanism of the thermal dehydrochlorination of poly(vinyl chloride) has been the subject of many studies in the general area of polymer degradation. A number of the important contributions in this area have been reviewed by Levy in two excellent publications.[1,2] The present paper deals with the identification of the volatile, hydrocarbon pyrolysis products resulting from the thermal degradation of PVC at 600°C in an inert (helium) atmosphere.

The objective of the current study was to obtain a complete profile of the degradation products from PVC resin and PVC plastisols. This study has acted as a starting point in an overall study of thermal degradation, combustion, and flammability of chlorinated polymers.

PREVIOUS WORK

Stromberg[3] has studied the thermal degradation of PVC in vacuum by first stripping the resin of HCl at temperatures up to 350°C for 30 min. The resulting residue was then heated at 400°C for 30 min and the volatile hydrocarbon products resulting from this second heating were identified via mass spectrometry. In this particular study, Stromberg identified approximately 25 hydrocarbon products.

Ohtani and Ihikawa[4] pyrolyzed PVC at 425°C in a nitrogen atmosphere and studied the resulting degradation products by infrared and ultraviolet spectroscopy. Their findings showed that: (*1*) the pyrolysis products (other than HCl) consisted of aliphatic and aromatic hydrocarbons, and (*2*) the types of pyrolysis products from PVC were a function of the stereoregularity (tacticity) in the undegraded polymer. Additional qualitative or quantitative measurements were not made.

Noffz et al.[5] degraded PVC in a high-frequency pyrolyzer and separated the degradation products by gas chromatography. Their findings revealed that the hydrocarbon degradation products consisted of only aromatic compounds; a volatile aliphatic hydrocarbon fraction was not identified.

Coleman and Thomas[6] have studied the combustion of PVC by thermally degrading the polymer in an excess of oxygen. Under the experimental conditions employed, the hydrocarbons formed as a result of polymer degradation were completely oxidized to carbon oxides. In addition to HCl, CO, and CO_2, a very trace amount (5 ppm) of carbonyl chloride was also identified.[7]

In a more recent study of the degradation of PVC in air, Boettner et al.[8,9] found that when PVC homopolymer and compounds were heated in air from ambient to 600°C, approximately 95% of the PVC was reacted to HCl, CO, and CO_2 (no phosgene above 0.1 ppm). The 5% hydrocarbon fraction consisted of 18 aliphatic and aromatic hydrocarbons.

Analogous degradation experiments of PVC plastisols (PVC plus a phthalate ester) revealed that the hydrocarbon fraction of the pyrolyzate increased due to products from thermal breakdown of the plasticizer. Characteristic degradation products derivable from the plasticizer alone were not formed.

INSTRUMENTATION AND PYROLYSIS TECHNIQUES

Thermolysis of PVC resin (Geon 103, Cl = 57.4%) was carried out by two general techniques. The first method involved heating the resin in the heated (325°C) inlet of our mass spectrometer (CEC model 21-103C) in order to obtain a mass spectrum of the total pyrolyzate.

The second, more detailed method consisted of degrading the resin in a pyrolysis–gas chromatograph–mass spectrometer (PGM) tandem system. Briefly, our PGM unit consists of an F & M Model 700 temperature-programmed gas chromatograph interfaced to the mass spectrometer through a molecular enricher.[10] A pyrolysis unit consisting of a radiant

Fig. 1. Schem
(helium) lines;
ling valve and (
cate the directi

type furnace
F & M gas sa
the gas samp
chromatograp
unit. The tw
the body of th
way, carrier g
chamber and
directed to ei
diagram of th
valve is presen
The results
of the mass s
chromatograp
chromatograp
separated on a
acenaphthalen
CRG) column
was also used
The plastisols
of plasticizer (
Samples of
gas flow of 60–

Since a stoic
heated at 600°
The problem o
lowing manne
chromatograp

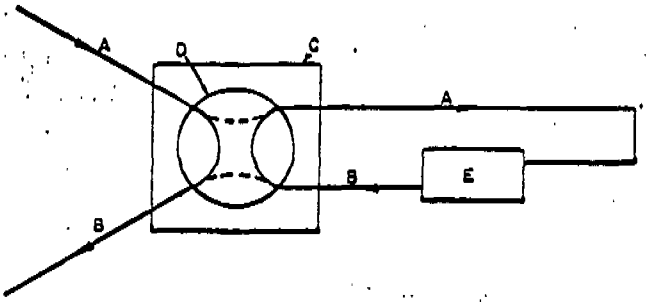


Fig. 1. Schematic of pyrolysis unit illustrating relative position of (*A*) carrier gas (helium) lines; (*B*) heated effluent lines; (*C*) oven containing; (*D*) F and M gas-sampling valve and (*E*) quartz pyrolysis chamber and radiant heat pyrolyzer.—Arrows indicate the direction of gas flow.

type furnace (Sargent & Co., Model S-30100), quartz chamber, and heated F & M gas sampling valve (Model GV-11) was constructed. Function of the gas sampling valve was to interface the pyrolysis chamber to the gas chromatograph and to permit on-line or off-line operation of the pyrolysis unit. The two gas chromatographic carrier gas lines were "looped" outside the body of the chromatograph through Tygon tubing connectors. In this way, carrier gas could be directed from the chromatograph to the pyrolysis chamber and the effluent line from the pyrolysis chamber could then be directed to either of the injection ports of the gas chromatograph. A diagram of the pyrolysis chamber, gas chromatograph, and gas sampling valve is presented in Figure 1.

The results from the pyrolysis experiments carried out in the heated inlet of the mass spectrometer indicated that in order to obtain a complete chromatographic separation of the pyrolysis products from PVC, two chromatographic columns would be required. Light gases (C_1–C_4) were separated on an 8-ft Porapak QS while the higher-boiling components (C_4 to acenaphthalene) were analyzed on a 20-ft × $^3/_{16}$ in. SE52 (10% on 80/100 CRG) column. This same combination of gas chromatographic columns was also used for the analyses of degradation products from PVC plastisols. The plastisols were prepared by fusing 100 parts of PVC resin with 60 parts of plasticizer (i.e., *o*-dioctyl phthalate) at 350°F for 5 min.

Samples of PVC resin and plastisols were pyrolyzed at 600°C in a carrier gas flow of 60–70 ml/min; sample sizes ranged from 10 to 20 mg.

HCl EVOLUTION DURING PYROLYSIS

Since a stoichiometric amount of HCl is released (58.3%) from PVC when heated at 600°C, over half of the degradation products, by weight, is HCl. The problem of chromatographic analysis of HCl was dealt with in the following manner. It was found that for analyses performed on the SE52 chromatographic column, the retention time of the HCl peak corresponded

approximately to the dead time of the column. This peak was fairly symmetrical and did not exhibit excessive bleeding.

However, with the Porapak column, HCl was found to bleed excessively. In order to correct this, the pyrolyzate was scrubbed of HCl by placing 4 Å molecular sieves in the heated (150°C) effluent line (Fig. 1, *B*) to the chromatograph. This eliminated the HCl and did not seem to remove any of the other gases. It was found, as a result of other work, that the sieves did have an affinity for short chain chloroalkanes under these conditions.

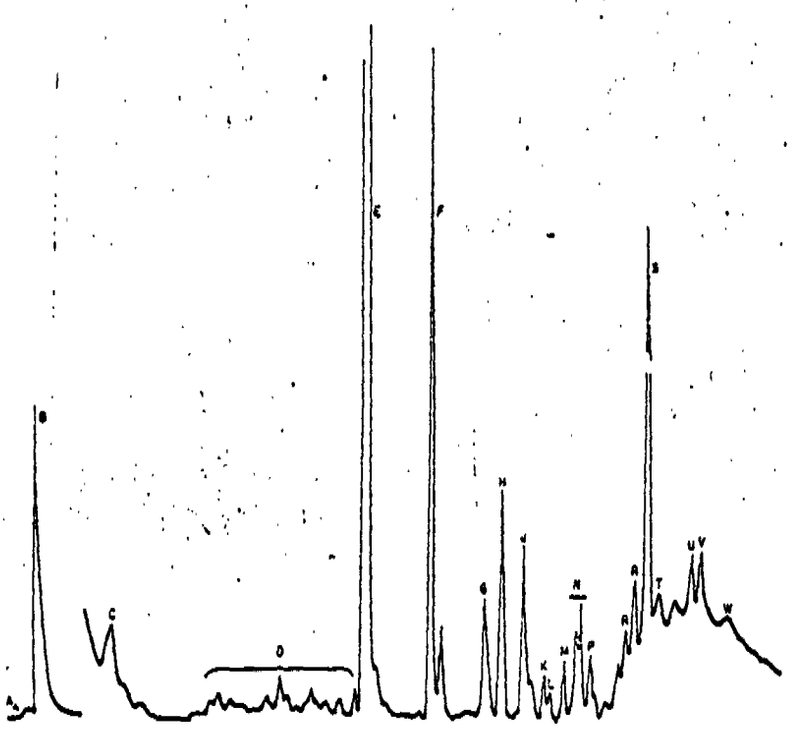


Fig. 2. Pyrogram of PVC resin from 20 ft × ⅛ in. 10% SE52 on 80/100 CRW chromatographic column. Lettered peaks refer to identifications in Table I.

Since these types of compounds are not evolved during the pyrolysis of PVC, this selectivity for chloroalkanes did not interfere with the results of the analysis.

In a typical pyrolysis experiment, 10–20 mg of PVC resin were precisely weighed into a 5.0 mm × 10 mm porcelain boat and loaded into the pyrolysis chamber along with a small magnet. The chamber was closed, the gas sampling valve was so positioned that the pyrolysis unit was on-line with the chromatograph, and the furnace was turned on. Once the temperature of the furnace reached 600°C (calibrated), the boat was moved, with the aid of

the magnet, into the hot zone of the pyrolysis chamber. In this way a typical pyrogram was recorded.

After the remains of the sample cooled down, the gas sampling valve was positioned for off-line operation.

While the gas-chromatographic analysis was being completed, the chamber (now off-line) was opened, and the sample boat was removed and weighed. This operation permitted the percentage char formation to be calculated. The measurement was not corrected for minor amounts of material which condensed at the end of the pyrolysis chamber.

PYROLYSIS OF PVC RESIN

Pyrolysis of PVC at 600°C in a helium atmosphere results in the complete removal of Cl as HCl (58.3%) from the backbone of the polymer. The resulting carbonaceous ash, devoid of chlorine, represents approximately 3–4% of the original polymer.

TABLE I
Identification of Components in Pyrogram (Fig. 2) of PVC

Peak identification	Components
A	CH_4,[a] CO,[a] CO_2,[a] C_2H_4,[a] C_2H_6[a]
B	HCl, C_3H_6,[a] C_3H_8[a]
C	Butane,[a] butene,[a] butadiene,[a] diacetylene[a]
D	C_5 and C_6 aliphatic and olefinic hydrocarbons
E	Benzene
F	Toluene
G	Chlorobenzene
H	Xylene
J	Allylbenzene
K	C_9H_{12}
L	C_9H_{12}
M	Indane
N	Indene, ethyltoluene
P	Methylindane
R	Methylindene
S	Naphthalene
T	Dimethylindane
U	Methylnaphthalene
V	Methylnaphthalene, acenaphthalene
W	Dimethylnaphthalene

[a] Separated and identified on an 8-ft Porapak QS.

Aside from a stoichiometric amount of HCl, the PVC pyrolyzate consists of a series of aliphatic, olefinic, and aromatic hydrocarbons. Only one chlorinated hydrocarbon, chlorobenzene, was found, and the yield of this component was well below 1 wt-%.

A typical pyrogram of PVC (SE52 column) is presented in Figure 2; component identifications are summarized in Table I. A similar analysis

was also carried out on the Porapak QS column. The components separated and identified in this analysis are noted in Table I.

The major components resulting from the pyrolysis of PVC are HCl, benzene, toluene, and naphthalene. In addition to these major products, an homologous series of aliphatic and olefinic hydrocarbons ranging from C_1 to C_4 are formed. This finding is in direct contrast to the results obtained by Nolfs. This difference may be attributed to differences in techniques since Nolfs degraded his samples with rf energy.

GAS CHROMATOGRAPHIC ANALYSIS OF HCl

The chromatographic peak from HCl can be used to quantify the amount of HCl released during the pyrolysis of PVC if the pyrolysis and chromatographic system is first "seasoned" with a slug of HCl gas. For example, in one experiment a series of PVC samples (10–20 mg) were pyrolyzed at 600°C and the gas-chromatographic areas of the resulting HCl peaks were recorded. (The gas chromatography column and pre-column were maintained at ambient temperatures throughout this experiment. Usually six to seven pyrolyses could be carried out before benzene began to

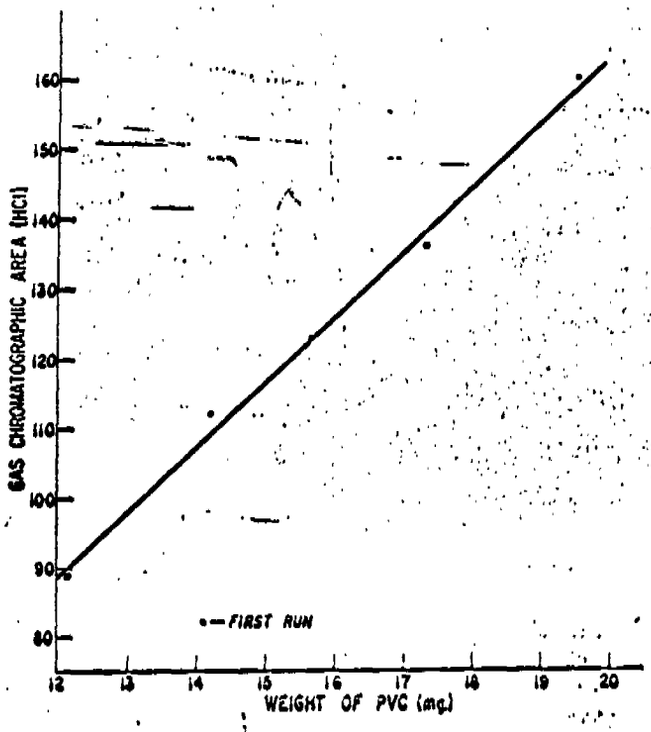


Fig. 3. Plot of HCl (gas-chromatographic area) vs. weight of PVC resin pyrolyzed at 600°C.

bleed from the column. Bleeding of minor amounts of other more volatile hydrocarbons did not interfere with the analyses).

A plot of HCl content (peak area) versus weight of resin pyrolyzed at 600°C is presented in Figure 3. Aside from the first run, all subsequent analyses provided a linear relationship between the two variables of HCl area and amount of resin pyrolyzed. The first run of HCl through the column seems to condition the apparatus by coating the walls with gaseous HCl. In subsequent runs, all of the HCl formed during pyrolysis, reaches the detector with little or no adsorption on the chromatographic walls.

This aspect of the pyrolysis of PVC is being further investigated in the direction of optimizing the technique for measuring the amount of HCl produced when PVC compounds and other chlorinated polymers are thermally degraded.

PYROLYSIS REPRODUCIBILITY

The demonstration of reproducibility in pyrolysis work is an important aspect of this technique. In order to meet this requirement, three pyrolysis

TABLE II
Composition (Gas-Chromatographic Area) of PVC Hydrocarbon Pyrolyzate

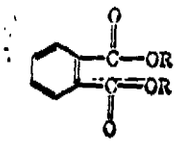
Component	Area, %		
	Run 1	Run 2	Run 3
CO	0.6	2.2	0.8
Methane	8.8	7.8	9.3
CO_2	0.4	0.3	0.2
Ethylene	3.5	3.5	3.8
Ethane	4.8	5.1	5.5
Propylene	2.0	2.6	3.0
Propane	3.0	1.0	2.3
Butane, butene	2.5	2.1	2.1
Butadiene, dimethylene			
C_5 and C_6 hydrocarbons	1.0	1.8	1.3
Benzene	51.2	50.8	50.1
Toluene	5.3	5.0	5.8
Chlorobenzene	1.1	1.1	1.3
Xylene	1.9	2.1	2.3
Allylbenzene	1.3	1.4	1.6
C_9H_{12}	0.4	0.5	0.5
C_9H_{12}	0.2	0.2	0.3
Indane	0.2	0.3	0.3
Indene	0.9	1.4	0.9
Ethyltoluene			
Methylindane	0.5	0.5	0.5
Methylindenes	1.1	1.3	1.0
Naphthalene	4.8	4.6	4.5
Dimethylindane	0.7	0.8	0.8
Methylnaphthalene	0.8	0.7	0.7
Methylnaphthalene	1.2	1.0	1.1
Acenaphthalene			

experiments were carried out in which various PVC (resin) samples were pyrolyzed at 600°C. (A dual analysis was carried out in each case, one for analysis on the SE52 chromatographic column, the other for analysis on the Porapak QS column.) The resulting gas-chromatographic peak areas of all components were recorded for the three pyrolysis experiments. These three analyses, summarized in Table II, demonstrate the quantitative and qualitative reproducibility of the technique.

The gas chromatographic peak areas reported in Table II closely reflect the mole per cent contents, thus an approximate quantitative analysis of the pyrolyzate from thermally degraded PVC is possible. It should be noted that the total hydrocarbon fraction corresponds to approximately 38% (weight) of the original PVC sample; the remaining 62% consists of HCl and a carbonaceous, chlorine-free ash. Benzene is the component of greatest concentration in the entire hydrocarbon fraction.

PYROLYSIS OF POLY(VINYL CHLORIDE) PLASTISOLS

Initial pyrolysis of PVC plastisols centered about a plastisol prepared by fusing 100 parts of PVC and 60 parts of *o*-(2-ethylhexyl) phthalate (DOP) at 350°F for 5 min. The scope of this initial study was then expanded to include a number of other PVC plastisols. The plasticizers used throughout this study were derived from *o*-phthalic acid:



The results of the initial study (PVC/DOP) revealed that the degradation products reflected both polymer and plasticizer thermolysis. Thus, the pyrogram could be used as a finger printing tool for identifying the specific plasticizer present in the plastisol.

The pyrolysis of the PVC/DOP plastisol was carried out at 600°C in a helium atmosphere; the resulting pyrogram (SE52 gas chromatography column) from this pyrolysis is presented in Figure 4. Peak identifications are summarized in Table III.

As previously mentioned, the pyrolysis products reflect polymer degradation (HCl, benzene, toluene, etc.) and plasticizer degradation (C_8 hydrocarbon, C_8 aldehyde, and phthalic anhydride). It is the presence of those components due to DOP fragmentation that provides the basis for using the plastisol pyrogram as a "fingerprinting" aid.

This fingerprinting capacity of pyrograms from typical PVC plastisols is illustrated in Figure 4. A series of seven pyrograms resulting from the pyrolysis of the following PVC plastisols is presented: (*B*) *o*-dihexylphthalate (DHP), (*C*) *o*-di-2-ethylhexyl-phthalate (DOP), (*D*) *o*-dicapryl phthalate (DCP), (*E*) *o*-diisodecyl phthalate (DDP), and (*F*) the mixed

ester butyl benzyl o-phthalate (BuBzP). The first pyrogram in Figure 4 is that of the resin without plastisol and is included for purposes of comparison. It should be noted that much of the detail (i.e., minor components) of these

TABLE III
Comparison of Gas-Chromatographic Areas of Degradation Products from PVC Resin and PVC Plastisol (DOP, 100/50)[a]

Degradation product	Area, %	
	Resin	DOP Plastisol
CO	0.6	1
Methane	8.8	3.3
CO_2	0.4	6.5
Ethylene	3.5	2.8
Ethane	4.8	4.6
Propylene	2.9	4.7
Propane	3.0	1.5
Butane, butene	2.5	5.2
C_3 and C_4 hydrocarbons (total)[b]	1.9	—
C_5H_{10}	—	1.0
Isoprene	—	1.1
2-Methyl-1-butene	—	2.0
3-Penten-1-yne	—	0.4
C_5 olefin (total)	—	1.6
Benzene	51.2	11.8
C_7 olefins	—	1.3
Toluene	5.3	2.6
C_8 olefins	—	24.7
Chlorobenzene	1.1	0.4
Xylene	1.9	0.7
Allylbenzene	1.3	—
C_9H_{12}	0.4	—
C_9H_{12}	0.3	—
2-Ethyl hexanal	—	1.4
Indane	0.2	—
Indene	—	—
Ethyltoluene	0.9	0.5
Methylindane	0.5	—
Methylindene	1.1	0.8
Naphthalene	4.8	1.2
Dimethylindane	0.7	—
Methylnaphthalene	0.8	—
Acenaphthalene	1.2	—
Methylnaphthalene	—	19.9 (minor)
Phthalic anhydride		(major)

[a] Area related to mole-%.
[b] Applicable only to degradation of resin.

pyrograms has been omitted through a judicious choice of attenuation settings on the gas-chromatographic recorder.[7] This was done for reasons of simplicity as the major peaks in each of the pyrograms provided adequate differences for purposes of fingerprinting.

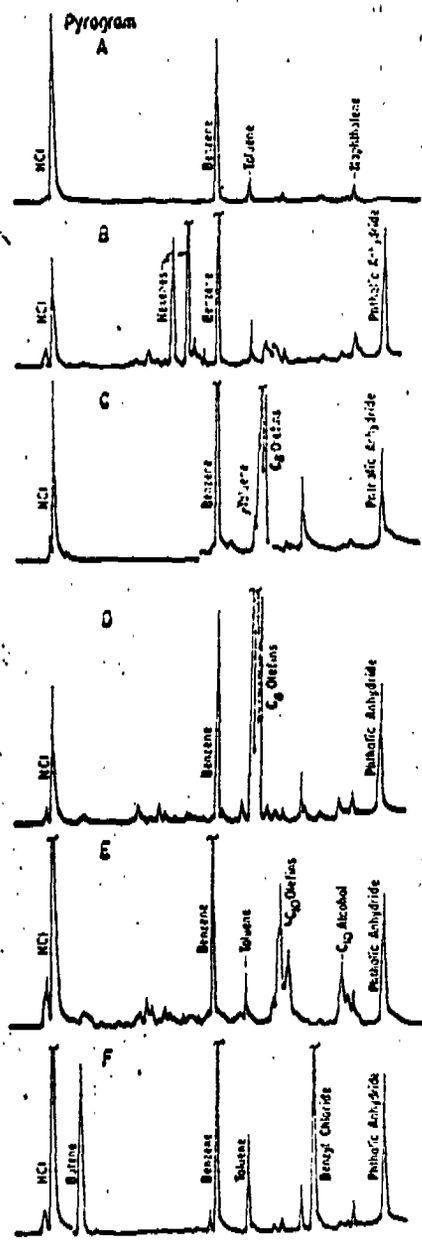


Fig. 4. Pyrograms of (*A*) PVC resin; (*B*) PVC/o-dihexyl phthalate; (*C*) PVC/o-di-2-ethylhexyl phthalate; (*D*) PVC/o-dicapryl phthalate; (*E*) PVC/o-diisodecyl phthalate; (*F*) PVC/o-butyl benzyl phthalate.

Detail
plastisol
have be
The fi
the maj
naphtha
contains
phthalic
The pyr
dihexyl
the aror
the olefi
plasticiz
Olefin
and sui
phthala
The
terestin
phthalic
the thre
already
ployed
fects th
these t
olefins
pyrolys
plastici
If it
cizers w
chroma
hydroly
ysis pr
The
of an u
the res
A C
present
vides a
The
benzyl
pyrolys
graph

* Low
† The
cept th
reflecti

Detailed qualitative analyses of all degradation products from the five plastisols (*B–F*) were not carried out; only the major degradation products have been identified.

The first pyrogram in the series (Fig. 4) indicates the relative location of the major degradation from PVC resin (i.e., HCl, benzene, toluene and naphthalene).* The second pyrogram (*B*), PVC/*o*-dihexyl phthalate, contains those peaks representing thermolysis of the plasticizer (hexene and phthalic anhydride) in addition to those from degradation of the polymer. The pyrogram of *o*-diisodecyl phthalate/PVC (F) is analogous to that of the dihexyl phthalate pyrograms: the presence of phthalic anhydride identifies the aromatic portion of the plasticizer while the position (and presence) of the olefin moiety (C_{10} in this case) identifies the aliphatic portion of the plasticizer.

Olefinic degradation products result from the thermal de-esterification and subsequent dehydration of the plasticizer. In one case (diisodecyl phthalate), an alcohol (C_{10}) was found among the degradation products.

The pyrograms of the two C_8 plastisols (DOP and DCP) provide an interesting case. Both pyrograms contain a C_8 aldehyde peak, the expected phthalic anhydride peak, and three C_8 olefin peaks. However, the ratio of the three olefin peaks is different in each of the two cases. Since it has already been demonstrated that the reproducibility of pyrolysis, as employed in this study, is excellent, this difference in isomer distribution reflects the difference in the two C_8 plasticizers. Further investigation of these two plastisols directed toward the identification of the specific C_8 olefins in each case was not carried out. The important point was that *pyrolysis–gas chromatography* could be used to distinguish the two isomeric plasticizers.

If it had been necessary to completely characterize these two C_8 plasticizers with respect to the aliphatic portion, it is obvious that pyrolysis–gas chromatography offers many advantages over a technique involving acid hydrolysis of the plasticizer followed by an analysis of the alcoholic hydrolysis products.

The pyrogram of the mixed ester (BuBzP) plastisol reveals the presence of an unexpected secondary reaction occurring during pyrolysis or during the resulting chromatographic analysis.

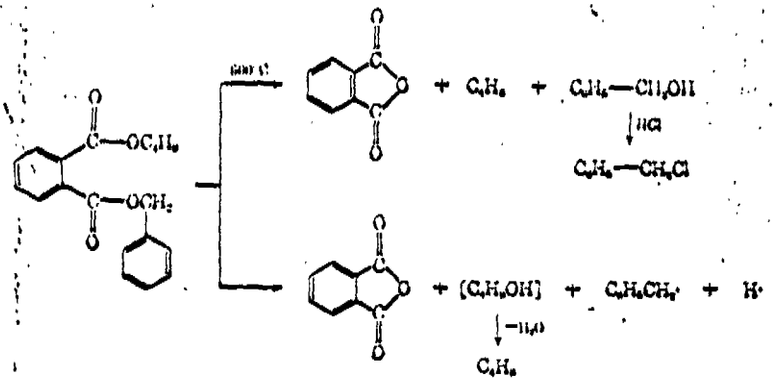
A C_4 olefin due to fragmentation of the butoxy portion of the ester is present, as expected. Pyrolysis of the $-OCH_2C_6H_5$ portion however, provides a unique case in that olefin formation via dehydration is not possible.

The pyrolysis products from this fragment ($-OBz$) were toluene† and benzyl chloride. Independent work in our laboratory, involving the pyrolysis of dibenzyl ether (HCl not rigorously excluded from gas-chromatograph lines or pyrolysis chamber) showed that this material produces the

* Lower-chain aliphatic products (CH_4, C_2H_4, etc.) are buried under the HCl peak.

† The *ratio of benzene/toluene* (peak height:peak height) in all of the pyrograms, except that of DBzP, was 0.5 ± 0.4; in the BuBzP pyrogram the ratio was 3.6, thereby reflecting an increase in toluene.

same pyrolysis products. These data suggest that dibenzyl ether may be formed from the pyrolysis of butyl benzyl phthalate. Secondary pyrolysis of this intermediate followed by reaction with HCl would give the observed pyrolysis products. On the other hand, this ether may not be an intermediate, in which case free radicals formed from the pyrolysis of BuBzP may scavenge HCl, thereby forming the observed products:



The question as to whether or not dibenzyl ether is an intermediate in the pyrolysis of butyl benzyl phthalate is not within the scope of this paper; it is noted, however, that a secondary reaction of the pyrolysis products from BuBzP with HCl is in operation and it is this reaction that is the source of the benzyl chloride.

SEMIQUANTITATIVE ANALYSIS OF PLASTISOL PYROLYSIS PRODUCTS

The gas-chromatographic analysis of the pyrolysis products from a PVC/DOP (100/60) plastisol are presented in Table III. Included in this summary is a similar analysis for the PVC homopolymer (resin) in the absence of plasticizer.

The pyrolysis products from the plasticizer (DOP) constitute the major portion of the total products, thereby exhibiting a dilution effect on those products solely from the resin. The exception to this is the increase in the amount of CO_2 in the plastisol pyrolyzate. This results from a secondary reaction of the plasticizer—loss of CO_2; the major degradation path of DOP is however, directed toward phthalic anhydride formation.

The increase in C_3 and C_4 hydrocarbon content (relative to the resin) and the appearance of C_7 olefin in the plastisol pyrolyzate is due to secondary cracking of the C_8 moiety. The precursor of this material is again the DOP plasticizer.

Additional experiments were carried out in which the pyrolysis of the DOP plastisol was performed under static (no helium flow) conditions. This was accomplished by placing the gas sampling valve in the "off-line" position. After a five minute pyrolysis time, the valve was returned to the

"on-line" pos
to the chroma
complete crac

Boettner' l
programmed
addition to a
ular weight
The overall t
and HCl, the
The presen
is applicable
the plastic i
undergoes t
Thus, in thi
phthalic ani
ticizer's deg
not grossly
ular quantit
eter.
Boettner'
as the plast
may flame (
The findi
bility are of

The author
Dannis, the i
the technical

1. D. W.
and Thermal
and Tech. In
2. D. A.
Thermal Oxi
inghouse for
3. Strom
4. S. Ohi
5. D. No
6. E. H.
7. E. H.
8. E. A.
9. E. A.
10. J. T.
11. H. H
Characteris

Received
Revised I

"on-line" position and the pyrolysis products were swept from the chamber to the chromatograph. Under these conditions, the C_6 olefins underwent complete cracking to lower chain olefins.

TOXICITY OF DEGRADATION PRODUCTS

Boettner[9] has shown that when plasticized PVC is degraded in air under programmed temperature conditions a number of organic molecules (In addition to a stoichiometric amount of HCl), very similar to the lower molecular weight hydrocarbons identified in the present study, are released. The overall toxicity, however, is related to the gross quantity of CO, CO_2 and HCl, the first of these having the greatest effect.[11]

The present pyrolysis work, having been carried out in the absence of air, is applicable to only one particular set of fire conditions: that case where the plastic is subjected to "shock" heating conditions where plasticizer undergoes thermal degradation rather than evaporation and oxidation. Thus, in this particular instance, the degradation products would contain phthalic anhydride, the level of which would be dependent upon the plasticizer's degradation to evaporation/oxidation ratio. This product would not grossly affect the toxicity of the degradation products since the particular quantity of CO_2, HCl, and most importantly CO determines this parameter.

Boettner's work most closely simulates actual burning conditions, that is, as the plastic is heated, HCl and plasticizer are boiled off, the plasticizer may flame (depending on the HCl content) and CO and CO_2 are produced.

The findings of the present study representing a special case of flammability are offered as a corollary to Boettner's work.

The author wishes to acknowledge the technical comments of L. B. Crider and M. L. Dannis, the instrument modifications suggested by R. A. Yount and J. Deliman, and the technical assistance of J. A. Nikora.

References

1. D. W. Levi, "Literature Survey on Thermal Degradation, Thermal Oxidation, and Thermal Analysis of High Polymers," June, 1963. Clearinghouse for Fed. Scien. and Tech. Info., U. S. Dept. of Commerce, AD423546.

2. D. A. Teetsel and D. W. Levi, "Literature Survey on Thermal Degradation, Thermal Oxidation and Thermal Analysis of High Polymers II," January 1966, Clearinghouse for Fed. Scien. and Tech. Info., U. S. Dept. of Commerce, AD631634.

3. Stromberg et al., *J. Polym. Sci.*, 35, 355 (1959).

4. S. Ohtani and T. Ishikawa, *Kogyo Kagaku Zasshi*, 65, 1617–22 (1962).

5. D. Nolfs, W. Benz, and W. Pfab, *Z. Anal. Chem.*, 235, 121 (1968).

6. E. H. Coleman and C. H. Thomas, *J. Appl. Chem.*, 4, 379 (1954).

7. E. H. Coleman, *Plastics*, 24, 416 (1959).

8. E. A. Boettner and B. Weiss, *Amer. Ind. Hyg. Assoc. J.*, 28, 535 (1967).

9. E. A. Boettner et al., *J. Appl. Polym. Sci.*, 13, 377 (1969).

10. J. T. Watson and K. Biemann, *Anal. Chem.*, 36, 1135 (1964).

11. H. H. Cornish, paper presented at Polymer Conference Series on Flammability Characteristics of Polymeric Materials, University of Detroit, June 19, 1969.

Received December 1, 1969
Revised December 31, 1969