BFGoodrich INTER-ORGANIZATION CORRESPONDENCE

TO	Dr. R. P. Lattimer Dr. J. B. Pausch	FIELD POINT OR DEPT. & BLDG. NO. Corporate Technical Support - Brecksville	DATE YOUR LETTER
FROM		FIELD POINT OR DEPT. & BLDG. NO. Research & Development Center- Brecksville	DATE THIS LETTER 1-24-83

SUBJECT

PUBLICATION APPROVAL

25-4561

The BFGoodrich Publications Committee has approved for publication the Abstract of your proposed paper entitled "Pyrolysis Studies of Chlorinated Poly(vinyl chloride)."

Our records indicate that the paper will be presented orally by Dr. Lattimer at the 31st Annual Conference on Mass Spectrometry and Allied Topics in Boston, Massachusetts, May 8-13, 1983. And the paper will be published in Macromolecules.

This is subject to approval of the final paper by the Publications Committee.

R. J. Fawcett/d

R. J. Fawcett

d
encls.

cc: Research Files, Brecksville - w/Manuscript and approval sheets
Public Relations, Akron - w/Manuscript
E. G. Fiorito - w/Manuscript
D. E. Ley - w/Copy of approval sheets

Messrs. K. C. Baranwal
J. W. Messerly
R. J. Meyer - 2 -
C. E. Wilkes
D. E. Ley - For SI Metric Conversion

This paper may be of interest to your division. If so, would you comment on the suitability for publication on the attached Request for Approval sheet and return to me.

If this paper is not relevant to your division, please return indicating no interest.

Promptness in reply will be appreciated.

R. J. Fawcett

d
Attachment

The R.J. Meyer recommendation is being followed by the ~~Authors~~.
Deane E. Ley
1/19/83

Approved by Chemical Group on condition that emphasis be taken off "Lightly Chlorinated", Revise title to "Pyrolysis Studies of Chlorinated Poly(vinyl Chloride) and change abstract as noted - PJMeyer 1/17/83

2072900

BFG05144

REQUEST FOR APPROVAL FOR PUBLICATION

Title of Paper Pyrolysis Studies of Lightly Chlorinated Poly(vinyl chloride)
Author(s) R. P. Lattimer, J. B. Pausch and H. L. C. Meuzelaar
Date January 5, 1983 Deadline Remarks

1. Why do you feel this paper is a worthwhile contribution to the technical literature?

It correlates analytical pyrolysis data with microstructural data (NMR) on CPVC. It is the first detailed analysis of a synthetic polymer using pyrolysis-mass spectrometry in combination with computerized pattern recognition techniques.

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4. What information in this article decreases BFGoodrich technical advantages over competitors and to what extent?

No technical advantage will be compromised. NMR structural characterization of these materials has already been published. The general analytical techniques used have also been published.

5. To which Research Report does this paper relate? (Please include Access No.)

R. P. Lattimer, Project 9101-81, 10/22/81, A.N. 25-4057;
R. P. Lattimer, IOC, 10/14/82.

6. In what ways is BFGoodrich using this information?

The techniques are used to characterize complex polymer systems.

7. What is the patent situation?

To our knowledge there is nothing in this report that is patentable.

8. Do you plan on giving this paper orally? Do you propose to publish it? Please indicate where and when.

Oral presentation by Lattimer at 31st Annual Conference on Mass Spectrometry and Allied Topics, Boston, May 8-13, 1983. Publication in Macromolecules.

9. Was this paper requested or volunteered? By Whom?

Volunteered by Lattimer.

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JAN 13 1983
R. J. FAWCETT

R P Lattimer J B Pausch H L C Meuzelaar
Signature of Author(s)

Signature of Author's Manager

20729003

BFG05145

Title of Paper Pyrolysis Studies of Chlorinated Poly(vinyl chloride)
Author(s) R. P. Lattimer, J. B. Pausch and H. L. C. Meuzelaar
Date February 28, 1983 Deadline Remarks to be presented May 8-13, 1983
Abstract approved January, 1983.

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J. R. Lindsay
3/7/83

Approved
3/7/83

R. Lattimer, Jim Pausch, H.L.C. Meuzelaar
Signature of Author(s)

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Susan E. Ley
Signature of Author's Manager

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approved R L Barnard 1/17/83

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Susan E. Lee
Signature of Author's Manager

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R P Lattimer J B Pausch H L C Meuzelaar
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Dean E. Ley
Signature of Author's Manager

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Dean E. Ley
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R. J. FAWCETT

R P Lattimer for J B Pausch H L C Meuzelaar
Signature of Author(s)

Dean E. Ley
Signature of Author's Manager

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B.F. GOODRICH

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Approved for Patent
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Signature of Author(s)

Signature of Author's Manager

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R. J. SAWCETT

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Volunteered by Lattimer.

Approved
Charles E. Wilkes
Corporate Research
7/8/83

R. P. Lattimer, H. L. C. Meuzelaar
Signature of Author(s)

Duane E. Ley
Signature of Author's Manager

20729010

BFG05152

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R Lattimer HLC Meuzelaar
Signature of Author(s)

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Susan E. Ley
Signature of Author's Manager

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R. J. FAWCETT

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Volunteered by Lattimer.

Approved Tin Group
Kurt Barnard 3/7/83

R Lattimer HLC Meuzelaar
Signature of Author(s)

Dean E. Ley
Signature of Author's Manager

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Approved - J. R. Lindsay 3/7/83

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R. Lattimer, Jim Pausch, H.C. Meuzelaar
Signature of Author(s)

Duane E. Ley
Signature of Author's Manager

20729013

BFG05155

Pyrolysis Studies of Chlorinated Poly(vinyl chloride)

Robert P. Lattimer* and Jerry B. Pausch,
The BFGoodrich Research and Development Center
9921 Brecksville Road, Brecksville, Ohio 44141 (U.S.A.)

and

Henk L. C. Meuzelaar,
Biomaterials Profiling Center, University of Utah,
391 South Chipeta Way, Research Park,
Salt Lake City, Utah 84108 (U.S.A.)

ABSTRACT

The thermal decomposition of chlorinated PVC has been studied by pyrolysis-gas chromatography (Py-GC), Py-GC-mass spectrometry (Py-GC-MS), and Curie point pyrolysis-mass spectrometry (Py-MS). It was found that the yield of chlorobenzene pyrolyzate as determined by Py-GC correlates well with the weight-percent chlorine in the polymer or with microstructure parameters determined by ^{13}C NMR. Py-MS data for several CPVC samples were studied by computerized pattern recognition techniques (factor analysis and canonical variate analysis). It was found that numerous Py-MS fragments (namely a number of aromatic and chloroaromatic hydrocarbons) are strongly correlated with increases in the chlorine content of the polymer. Aliphatics and aromatics with more aliphatic character are negatively correlated with increasing chlorine level in the polymer. Py-MS with computerized statistical analysis holds considerable potential for characterizing the composition and studying thermal decomposition mechanisms in synthetic polymers.

INTRODUCTION

The thermal decomposition behavior of chlorinated poly(vinyl chloride), CPVC, has been the subject of several studies. Berticat prepared CPVC with a high chlorine level (73.2 wt.-% Cl) and found that CPVC was more thermally stable than PVC and that the principal volatile pyrolyzate was hydrogen chloride.[1] In later work Berticat reported thermogravimetric (TGA) results that showed a two-phase thermal decomposition for CPVC (73-74% Cl).[2] The first phase (~270 - 300°C) was mostly dehydrochlorination, and the second phase at higher temperatures was characterized by the evolution of chlorine-containing hydrocarbons. The greater thermal stability observed for CPVC as compared to PVC was attributed in part to crosslinking reactions.[2] Tsuge *et al.* studied a series of CPVC's with chlorine contents up to 73.2% by pyrolysis-gas chromatography (Py-GC).[3] The volatile pyrolyzates detected at 460°C were benzene, toluene, naphthalene, chlorobenzene, dichlorobenzenes (three isomers), trichlorobenzenes (three isomers), and tetrachlorobenzenes (three isomers). Tsuge *et al.* investigated the *relative* yields of these pyrolyzates as a function of the degree of chlorination. At "low" chlorine levels (up to ~62%), the relative benzene concentration decreased, while the chlorobenzene increased. The chlorobenzene concentration reached a maximum at ~64% chlorine, and then decreased as di- and trichloro compounds became dominant. The Py-GC results were used to deduce microstructural information regarding the CPVC samples.

In more recent work Liebman *et al.* studied the thermal decomposition and smoke evolution of PVC and CPVC. Electron spin resonance measurements demonstrated that free radicals are present during dehydrochlorination.[4] It was suggested that the better stability of CPVC compared to PVC was due to long

sequences of -CHCl- units in the polymer.[5] The better crosslinking (char forming) properties of CPVC as compared to PVC were also noted.[5] Liebman et al. also studied the evolution of smoke from burning PVC and CPVC.[6] A steady decrease in smoke evolution was observed as the chlorine level was increased. It was concluded that smoke was high in (low-chlorine) polymers because these materials evolved larger quantities of benzene and chlorobenzene - both of which burn with a smoky flame. More highly chlorinated PVC's evolve di-, tri-, and tetrachlorobenzenes upon pyrolysis; these aromatics yield less smoke upon burning.[6]

Interpretation of results from earlier pyrolysis/combustion experiments[3,6] was somewhat hampered by the lack of definitive microstructural data for the CPVC samples studied. ^{13}C NMR has recently made great progress in defining the microstructural units in CPVC and related polymers.[7-9] We have examined by Py-GC and Py-MS a series of chlorinated PVC's that have also been characterized by ^{13}C NMR.[9] Our primary objective was to determine if correlations could be made between the NMR and pyrolysis data. A secondary objective was to determine if Curie point Py-MS in combination with pattern recognition techniques could differentiate CPVC samples with varying chlorine contents. This report describes our preliminary results and conclusions.

EXPERIMENTAL

CPVC samples. The chlorinated PVC's ($\lesssim$ 61 wt.-% Cl) were prepared by solution photochlorination of Geon® 103EP PVC (The BFGoodrich Company) in tetrachloroethane at 80°C. The samples and numbering system are the same as described in the NMR study.[9]

Py-GC and Py-GC-MS. In our study five of the seven NMR samples[9] were analyzed by pyrolysis-gas chromatography (Py-GC). NMR characterization data along with chlorobenzene pyrolyzate yields are given in Table I. 40 μg of polymer was deposited on the ribbon pyrolysis probe from tetrahydrofuran solution. After evaporation of the solvent, the samples were pyrolyzed at 600°C for 20 s (temperature rise time ~8 ms) in helium atmosphere using a Chemical Data Systems Model 100 Pyroprobe. The pyrolyzates were separated with a 40 m Carbowax 20M fused silica capillary column. A Varian 3700/CDS 111 GC-microprocessor system (The BFGoodrich Company) was used with flame ionization detector. The capillary injector split ratio was 50/1. Calibration was achieved using injections of chlorobenzene in n-pentane solution (external standard method).

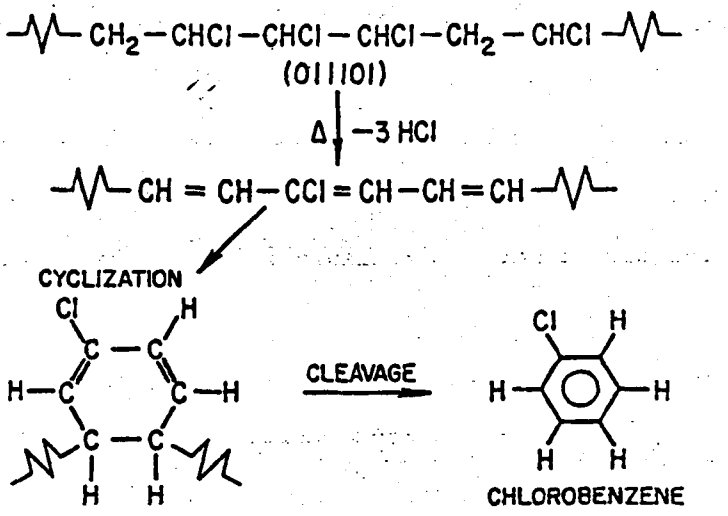
Qualitative identification of pyrolyzates was achieved by Py-GC-mass spectrometry, using a 40 m Carbowax 20M glass capillary column for separation. A Varian 3700/Finnigan MAT 311A/Finnigan Incos 2400 GC-MS-DS (The BFGoodrich Company) was used. Figure 1a shows the mass pyrogram for sample 1 (PVC), and Figure 1b shows sample 7 (CPVC). A trace of chlorobenzene appeared in sample 1, while several chloroaromatics appeared in sample 7 (chlorobenzene is the largest).

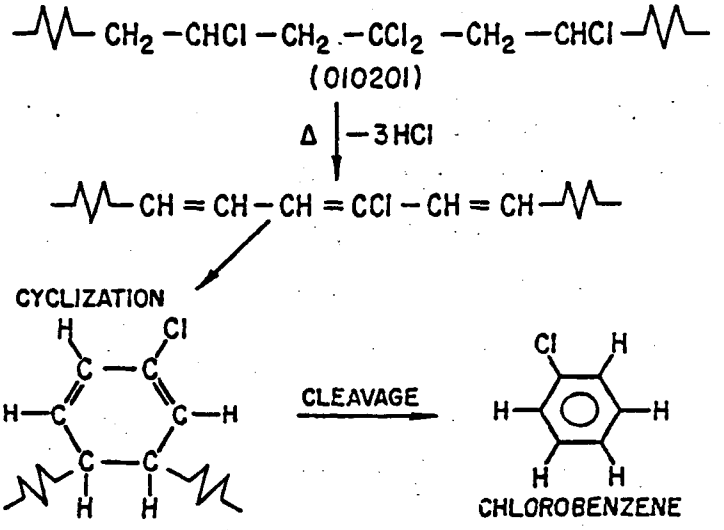
Py-MS. Six of the NMR samples[9] were also analyzed by Curie point Py-MS using an Extranuclear 5000-1 system (The University of Utah). About 4 μg of polymer was applied by microsyringe to the pyrolysis wire from tetrahydrofuran solution and air-dried under gentle rotation of the wire. Each sample was analyzed in triplicate. Py-MS conditions were as follows: Curie point temperature 610°C, temperature rise time 5 s, total heating time 10 s, reaction tube directly in front of the ion source (no expansion chamber used), electron energy setting 11 eV, mass range scanned m/z 25-240, scan rate 2000 amu/s, total scan time ~25 s. For each sample a single integrated spectrum was recorded. Spectra for sample 1 (PVC, Figure 2a) and sample 7 (CPVC, Figure 2b) are included.

Py-MS data processing. Computerized processing of the Py-MS data involved the use of spectrum calibration and normalization procedures described elsewhere,[10] as well as multivariate statistical analysis routines available in the Statistical Package for the Social Studies (SPSS).[11] Multivariate analysis consisted of principal component analysis of the complete Py-MS data matrix followed by canonical variate analysis of the correlations between the nine most significant (eigenvalues > 1.0) principal components (factors) and the chlorine content of the CPVC samples as determined by ^{13}C NMR.[9] Finally, the canonical variate "spectrum" was calculated according to a procedure described by Windig et al.[12]

RESULTS AND DISCUSSION

Chlorobenzene pyrolyzate yield. It was of interest to determine whether the yield of chlorobenzene as a pyrolyzate could be used as an indicator of the level of chlorine in CPVC. Only a trace of chlorobenzene is observed as a pyrolyzate in pyrolysis gas chromatography of PVC itself (Figure 1 and Table I). As the amount of chlorine in CPVC increases, the yield of chlorobenzene pyrolyzate, as detected by Py-GC, increases in a regular manner (Table I). The correlation of chlorobenzene pyrolyzate yield with Schöniger %-Cl is not at all good, since the Schöniger method is only accurate to ~±0.5%. Chlorobenzene correlation with %-Cl by ^{13}C NMR is nearly linear (Figure 3, correlation coefficient .988), but a better linear correlation is obtained by plotting chlorobenzene yield versus mole-% (111) + (020) structures from NMR (Figure 4, correlation coefficient .999). This linear correlation is consistent with established PVC decomposition pathways,[13-15] since either (111) or (020) structures can lead to chlorobenzene formation:


CH2–CHCl–CHCl–CHCl–CH2–CHCl
(011101)
Δ
–3 HCl
CH=CH–CCl=CH–CH=CH
CYCLIZATION
CLEAVAGE
CHLOROBENZENE


CH2–CHCl–CH2–CCl2–CH2–CHCl
(010201)
Δ
–3 HCl
CH=CH–CH=CCl–CH=CH
CYCLIZATION
CLEAVAGE
CHLOROBENZENE

We would expect this linear relationship to hold up to the point at which dichlorobenzene formation starts to become important compared to chlorobenzene. This transition is apparently ~61-62%-Cl.[3]

Py-MS correlations. The largest pyrolyzate peaks in the Curie point pyrolysis mass spectra (Figures 2 a,b) were m/z 36-38 $[HCl]^{+\cdot}$ and m/z 78 $[C_6H_6]^{+\cdot}$. Ions from residual tetrahydrofuran solvent (m/z 72-71-42) were also prominent in most samples; these peaks were ignored in the pattern recognition analyses. Some samples also showed appreciable $[SO_2]^{+\cdot}$ (m/z 64) from an unknown source.

The regular increase of chlorobenzene yield with increasing %-Cl is quite apparent in the Curie point Py-MS data. A bivariate plot of m/z 112 $[C_6H_5{}^{35}Cl]^{+\cdot}$ versus m/z 114 $[C_6H_5{}^{37}Cl]^{+\cdot}$ is given in Figure 5 (correlation coefficient .995). Note that appreciable intensities of m/z 112 and 114 were observed even for sample 1 (PVC), which yields only a trace of chlorobenzene pyrolyzate. These "baseline" intensities are due mainly to small amounts of hydrocarbon pyrolyzates (C_8H_{16} and C_8H_{18}).

A plot of the relative intensity of (m/z 112 + m/z 114) versus mole-% (111) + (020) is shown in Figure 6. The graph shows some curvature (correlation coefficient .943). This nonlinearity is apparently due to the fact that relative, rather than absolute, intensities of (m/z 112 + 114) have been plotted. Since the overall yield of volatile pyrolyzates in CPVC decreases as the chlorine level increases,[6] we should not expect Figure 6 to give a good linear correlation.[3]

As known from the literature[3] as well as evidenced by the chromatogram in Figure 1b, several chloroaromatic compounds in addition to chlorobenzene can be found as CPVC pyrolyzates. Since the intensities of such chloroaromatic species in the pyrolysis mass spectra of CPVC samples may be expected to correlate more or less strongly with chlorine content (as shown in Figures 5 and 6 for chlorobenzene), multivariate statistical analysis methods[10-12] can be used to identify these correlated peak series. Figure 7 shows the correlation between the canonical variate function calculated from the Py-MS data and the chlorine content values derived from NMR data.[9] As described in the Experimental section, this canonical variate function was calculated in the space described by the nine most significant principal coordinates (factors) of the Py-MS data using the canonical variate routine in the SPSS program.[11-12] Only peaks in the range m/z 78-177 were included in this calculation because of limitations in the size of the data matrix which can be handled by the program. The high correlation coefficient (0.995) and the sizable fraction (34.0%) of total variance in the Py-MS data set explained by the canonical variate function demonstrate that differences in chlorine content are among the most pronounced tendencies in the spectral patterns.

Because of the very limited size of the present set of samples no attempt was made to test the reliability of the canonical variate function for indicating the chlorine content of unknown samples. However, apart from its potential usefulness as a quantitative tool, the canonical variate function also enables the visualization of ion signals most strongly correlating with changes in chlorine content. Figure 8, shows a canonical variate spectrum calculated according to Windig et al.[12] The spectrum is dominated by chlorobenzene signals (m/z 112-114), but several other chloroaromatic signals are apparent at

m/z 126-128 (chlorotoluene), m/z 138-140 (chlorostyrene), m/z 150-152 (chloroindene), and m/z 162-164 (chloronaphthalene); most of these were also observed by Py-GC-MS (Figure 1b). In addition, a pronounced series of nonchlorinated aromatic pyrolyzates is also present - m/z 78 (benzene), m/z 92 (toluene), m/z 104 (styrene), m/z 106 (C_2 alkylbenzenes), m/z 116 (indene), m/z 128 (naphthalene), m/z 142 (methylnaphthalenes), m/z 154 (biphenyl/acenaphthene), m/z 156 (C_2 alkylnaphthalenes), m/z 166 (fluorene), and m/z 168 (methylbiphenyls/methylacenaphthenes). A final peak that shows a positive correlation is m/z 87, which we believe is an artifact due to degraded (oligomerized) tetrahydrofuran solvent.

Several hydrocarbon peaks are also observed on the negative side of the canonical variate spectrum (Figure 8). These compounds are either unsaturated aliphatics or else aromatics with appreciable aliphatic character. It is probable that lower molecular weight aliphatic hydrocarbons would also appear on the negative side of the spectrum, but the canonical variate analysis did not include mass numbers less than m/z 78.

Overall our results suggest that the CPVC pyrolyzates can be divided into three categories with respect to their formation tendencies:

1. Chloroaromatic compounds increase in both relative and absolute abundance as the chlorine level in the polymer increases. This was documented in earlier work[3,6] and has been confirmed in our studies.

2. Pure conjugated aromatic hydrocarbons and aromatics with small (C_1 - C_2) aliphatic side groups increase in <u>relative</u> abundance as the chlorine level

increases. Other work shows that in absolute abundance these compounds actually decrease with increasing chlorine level.[3,16]

3. Aliphatics and aromatics with more aliphatic character decrease in both relative and absolute abundance with increasing chlorine level in the polymer.

Our results show that as the chlorine level in the polymer increases, the volatile hydrocarbon pyrolyzates exhibit an overall decrease in hydrogen-to-carbon ratio. There are three possible explanations for this decrease in hydrogen in the volatile pyrolyzates: (1) there is less hydrogen available in the polymer; (2) more hydrogen is used to form HCl; and (3) more hydrogen remains in the polymer residue as char. Explanation (1) is certainly operative for CPVC, since for every chlorine atom added to the polymer one hydrogen atom is lost. Explanation (2) is also operative, since presumably more HCl is formed from the polymer during pyrolysis as the chlorine level increases. The HCl pyrolyzate yield as a function of polymer chlorine level has apparently not been the subject of careful study, however. Explanation (3) is probably not valid, since chars are generally very deficient in hydrogen.

While PVC itself produces little char during thermal decomposition, addition of chlorine to the polymer results in a steady increase in char residue.[6,17] This implies that crosslinking mechanisms not significant in PVC become important as more chlorine is added to the polymer. These mechanisms may involve intermolecular HCl elimination, Diels-Alder reactions, and various free radical processes.

These preliminary results suggest that Py-MS with computerized statistical analysis holds considerable potential for characterizing the composition and studying thermal decomposition mechanisms in chlorine-containing polymers. Further studies are in progress that should help to elucidate the thermal decomposition behavior of CPVC in more detail.

Acknowledgment. Appreciation is expressed to The BFGoodrich Company for support of this work. W. Windig and A. M. Harper (University of Utah) assisted with the computerized statistical analysis, and W. H. McClennen (University of Utah) performed the Curie point Py-MS experiments. I. Sockis and R. E. Harris (The BFGoodrich Company) assisted with the Py-GC and Py-GC-MS experiments. Helpful discussions with E. D. Dickens, Jr., G. S. Huvard, R. A. Komoroski, W. J. Kroenke, M. H. Lehr, and R. G. Parker (The BFGoodrich Company) are appreciated. S. A. Liebman (Chemical Data Systems, Inc.) is also acknowledged for encouraging us to work on this project.

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TABLE I. Chlorobenzene Pyrolyzate Yield and Other Characterization Data for Lightly Chlorinated PVC's.

Sample No.	% Cl[a]	% Cl[b] (NMR)	mol %[b] (111)	mol %[b] (020)	wt.-%[c] Chlorobenzene
1	56.2	56.8	0.0	0.0	~0.[d]
2	56.7	57.3	1.1	0.0	0.081±0.012
3	57.8	57.7	1.7	0.0	0.15±0.04
4	58.3	58.7	3.3	0.5	nd[e]
5	58.0	59.5	4.0	0.5	nd
6	57.9	60.1	5.6	0.6	0.48±0.07
7	59.4	60.6	7.1	1.4	0.69±0.07

[a] Schöniger oxygen flask method (data repeated from reference 9).

[b] ^{13}C NMR (from reference 9).

[c] Pyrolyzate yield (based on weight of polymer). Standard deviations are given from multiple runs.

[d] Trace of chlorobenzene observed by Py-GC-MS.

[e] Not determined.

Pyrolysis Studies of ~~Lightly~~ Chlorinated Poly (vinyl chloride)

by

R. P. Lattimer and J. B. Pausch
The BFGoodrich Research and Development Center
Brecksville, Ohio 44141

and

H. L. C. Meuzelaar
Biomaterials Profiling Center, University of Utah
Salt Lake City, Utah 84108

ABSTRACT

The thermal decomposition of lightly chlorinated PVC has been studied by pyrolysis-gas chromatography (Py-GC), Py-GC-mass spectrometry, and Curie point Py-MS. It was found that the yield of chlorobenzene pyrolyzate as determined by Py-GC correlates well with the weight-percent chlorine in the polymer or with microstructure parameters determined by ^{13}C NMR. Py-MS data for several CPVC samples were studied by computerized pattern recognition techniques (factor analysis and canonical variate analysis). It was found that numerous Py-MS fragments (namely a number of aromatic and chloroaromatic hydrocarbons) were strongly correlated with changes in chlorine content in the polymer. Py-MS with computerized statistical analysis holds considerable potential for characterizing the composition and studying thermal decomposition mechanisms in synthetic polymers.

TO	FIELD POINT OR DEPT. & BLDG. NO.	DATE YOUR LETTER
Dr. D. E. Ley	Director, Corporate Technical Support	
FROM	FIELD POINT OR DEPT. & BLDG. NO.	DATE THIS LETTER
	Research & Development Center- Brecksville	3-17-83

SUBJECT

PUBLICATION APPROVAL

The BFGoodrich Publications Committee has approved for publication the paper entitled "Pyrolysis Studies of Chlorinated Poly(vinyl chloride)" by Messrs. R. P. Lattimer, J. B. Pausch and H. L. C. Meuzelaar.

Our records indicate that the paper will be presented orally by Dr. Lattimer at the 31st Annual Conference on Mass Spectrometry and Allied Topics in Boston, Massachusetts, May 8-13, 1983. And the paper will be published in Macromolecules.

R. J. Fawcett/d

R. J. Fawcett

d
encls.

cc: Research Files, Brecksville - w/Manuscript and approval sheets
Public Relations, Akron - w/Manuscript
N. W. Shust - w/Manuscript

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The BFGoodrich Company
Research and Development Center
9921 Brecksville Road
Brecksville, Ohio 44141
216-447-5201

Robert J. Fawcett
Vice President
Research and Engineering

March 17, 1983

Dr. Robert P. Lattimer
R&D Associate
Corporate Technical Support
Brecksville, Ohio

Dear Bob,

I am pleased that the paper entitled "Pyrolysis Studies of Chlorinated Poly(vinyl chloride)" that is co-authored with Messrs. J. B. Pausch and H. L. C. Meuzelaar has been approved by the BFGoodrich Publications Committee.

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Sincerely,

Bob Fawcett

RJF/d

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Research and Development Center
9921 Brecksville Road
Brecksville, Ohio 44141
216-447-5201

Robert J. Fawcett
Vice President
Research and Engineering

March 17, 1983

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Corporate Technical Support
Brecksville, Ohio

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Sincerely,

Bob Fawcett

RJF/d

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Figure I. CAPILLARY MASS PYROGRAMS.

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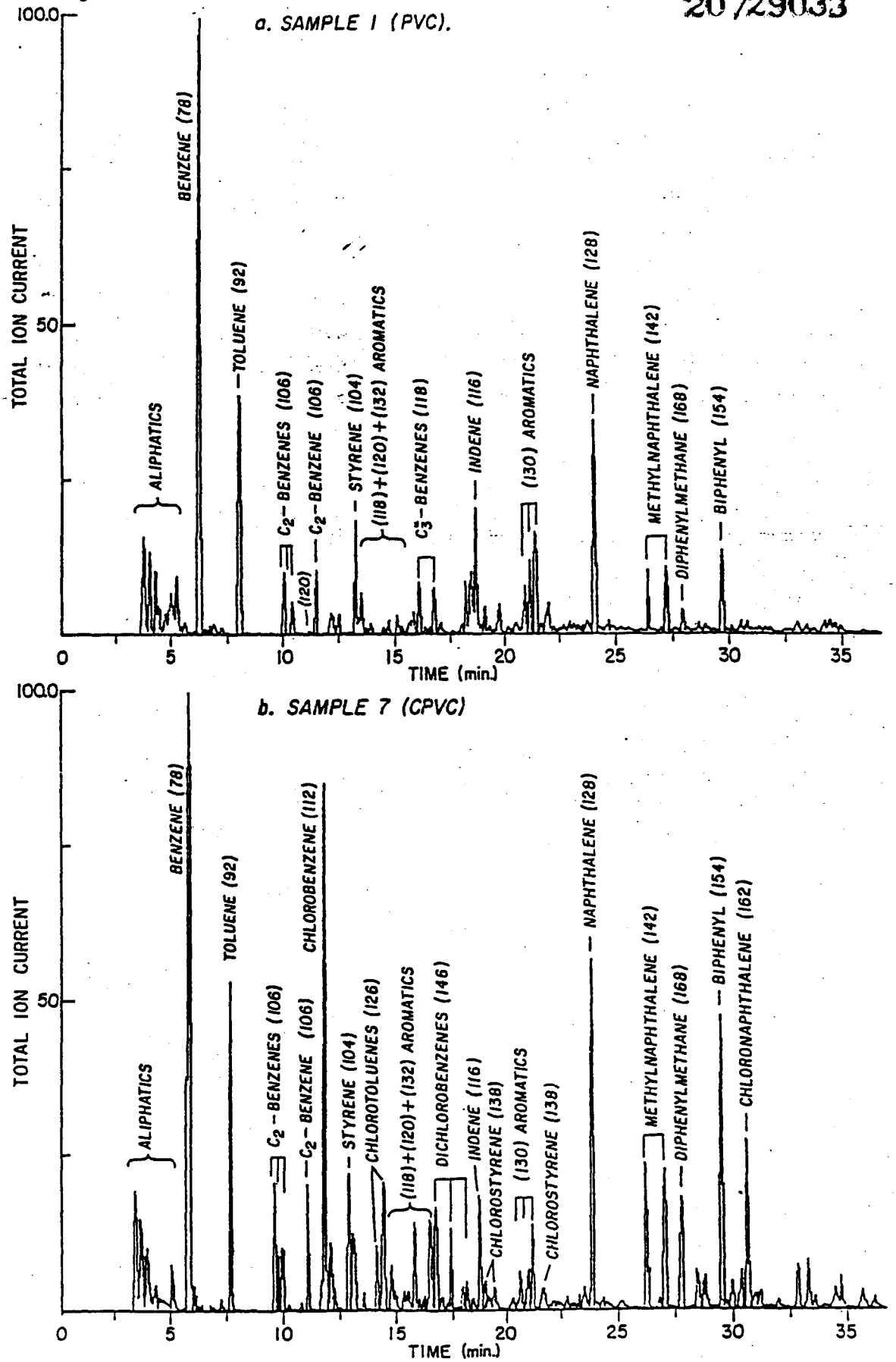

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Figure 2. CURIE POINT PYROLYSIS MASS SPECTRA.

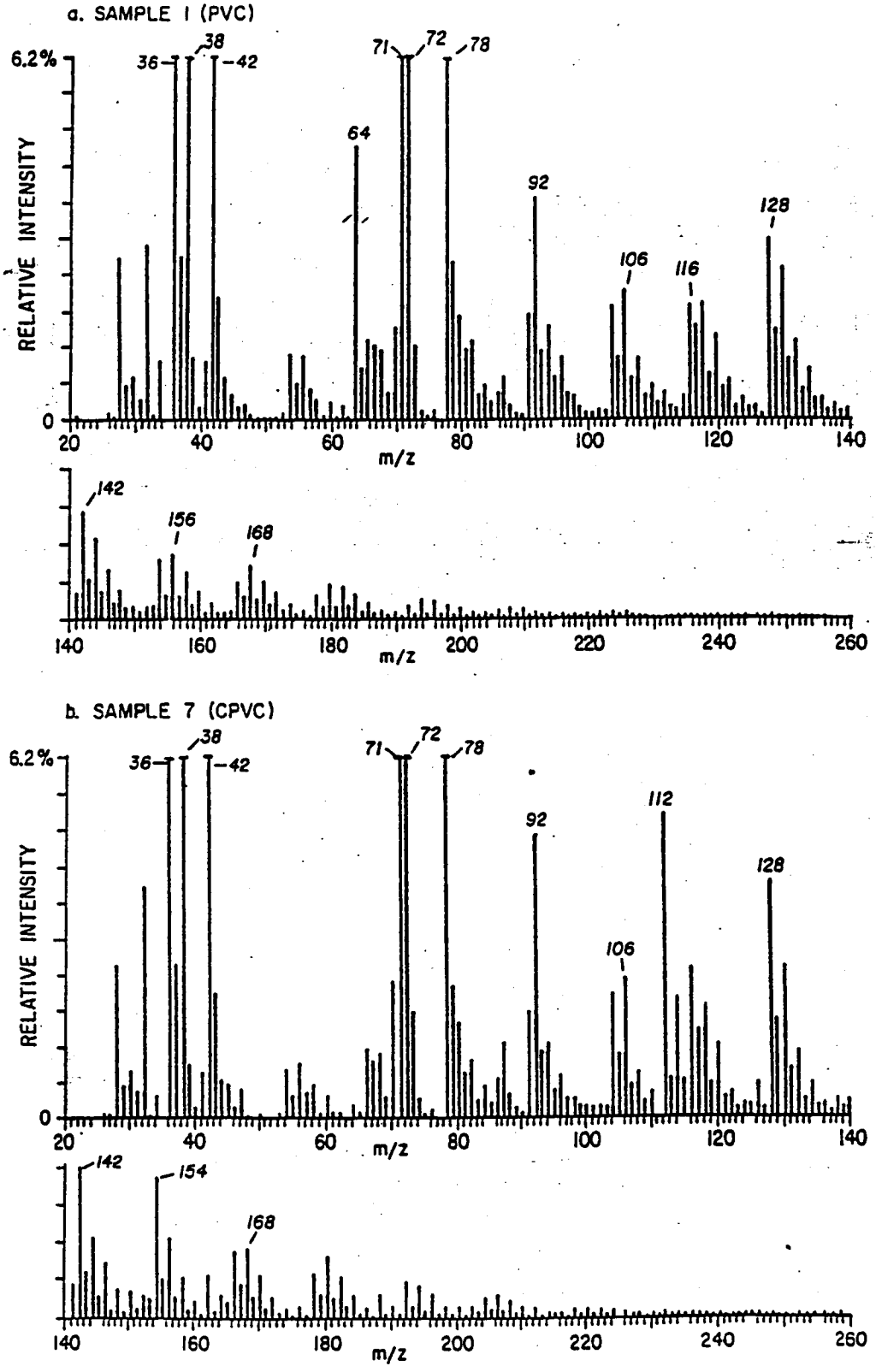
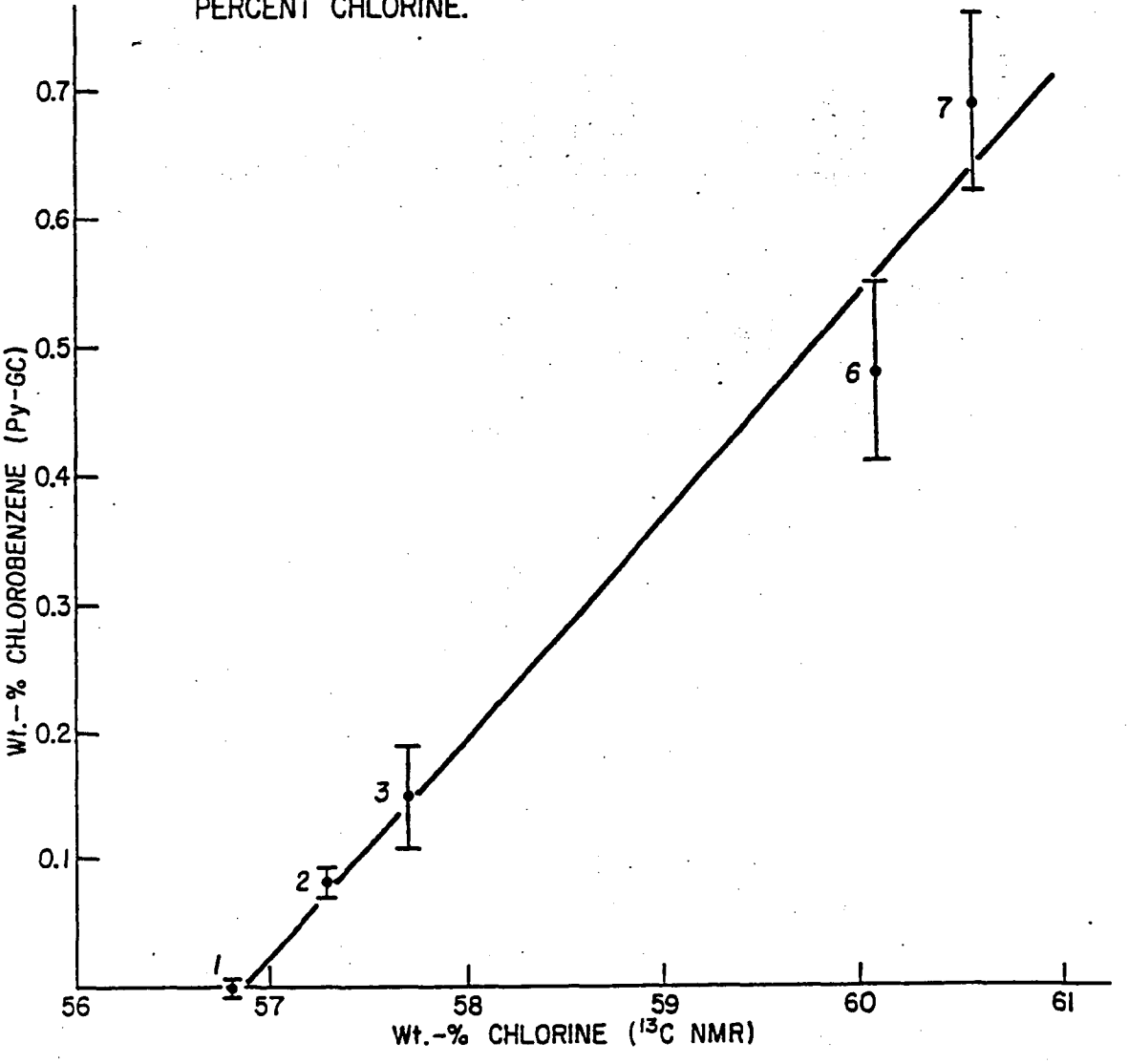


Figure 3. CHLOROBENZENE PYROLYZATE YIELD (Py-GC) versus PERCENT CHLORINE.



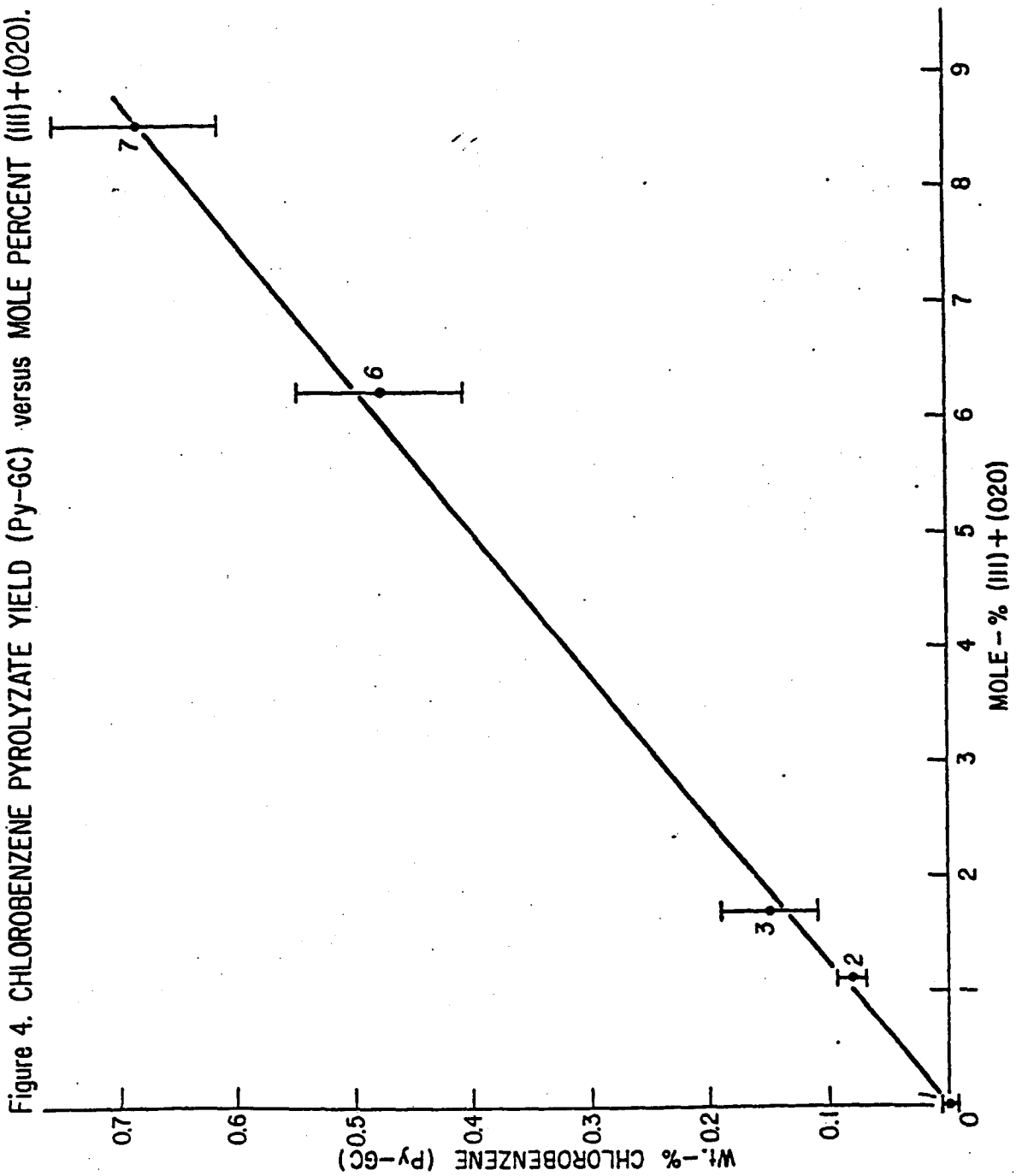


Figure 4. CHLOROBENZENE PYROLYZATE YIELD (Py-GC) versus MOLE PERCENT (111)+(020).

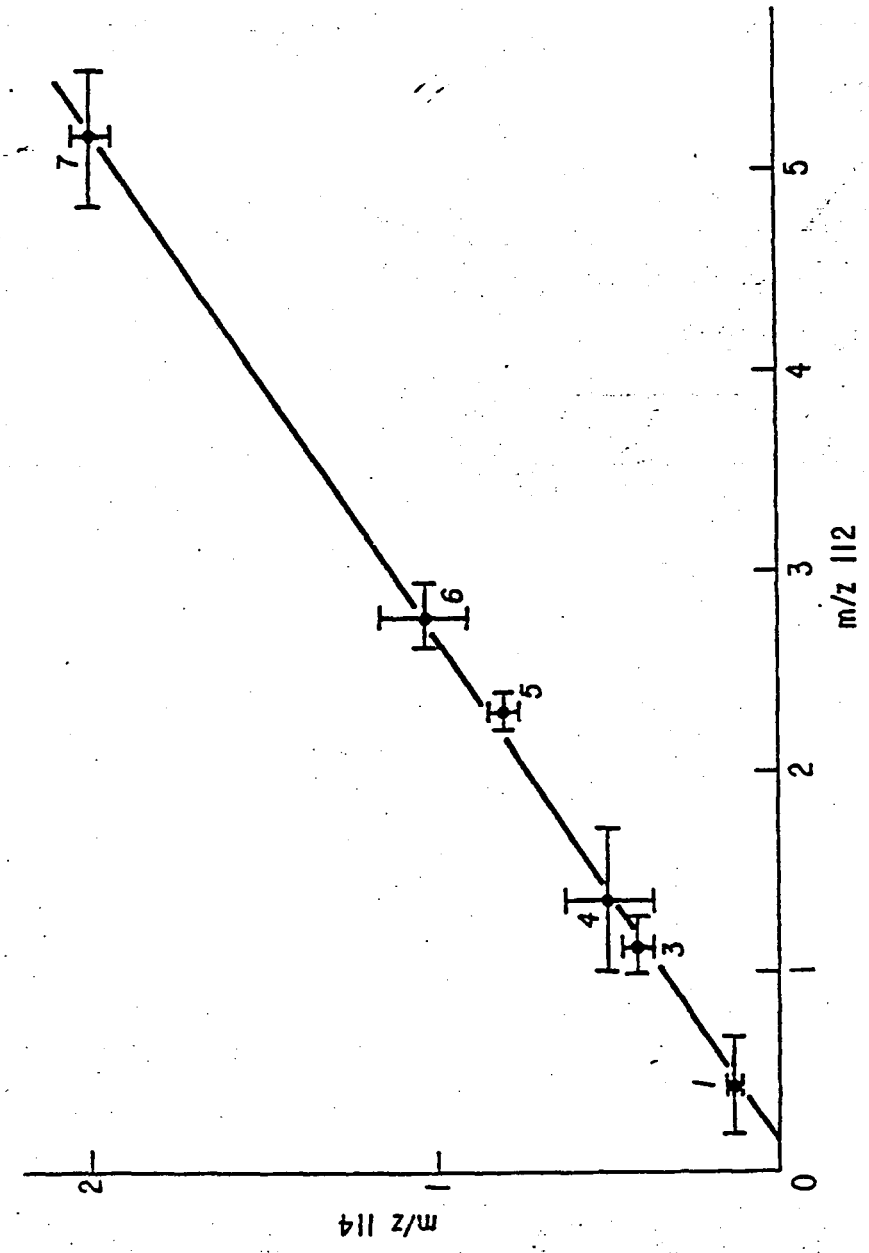
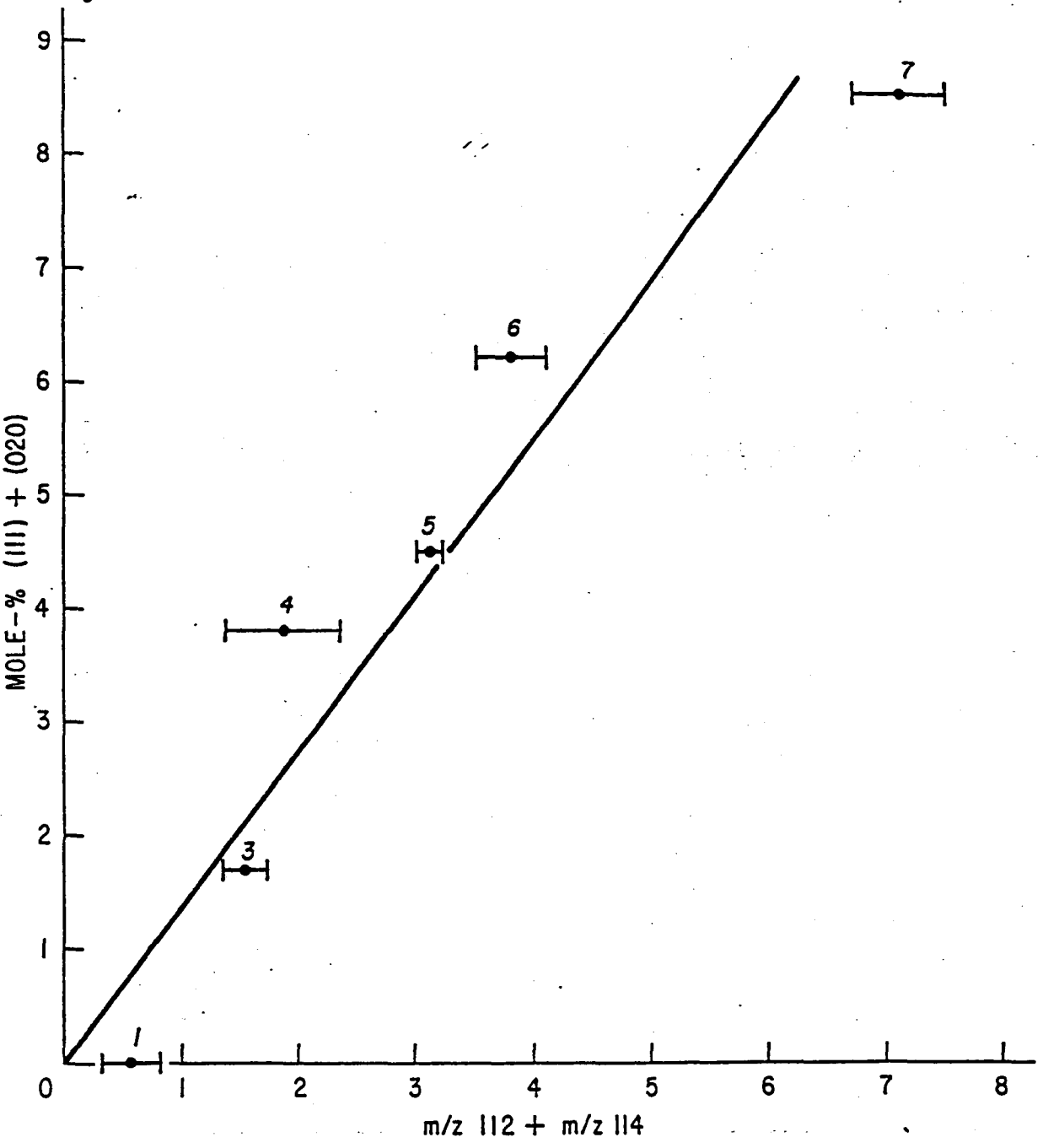


Figure 5. BIVARIATE PLOT (Py-MS) of m/z 112 and m/z 114.

Figure 6. MOLE-PERCENT (111) + (020) versus (m/z 112 + m/z 114).



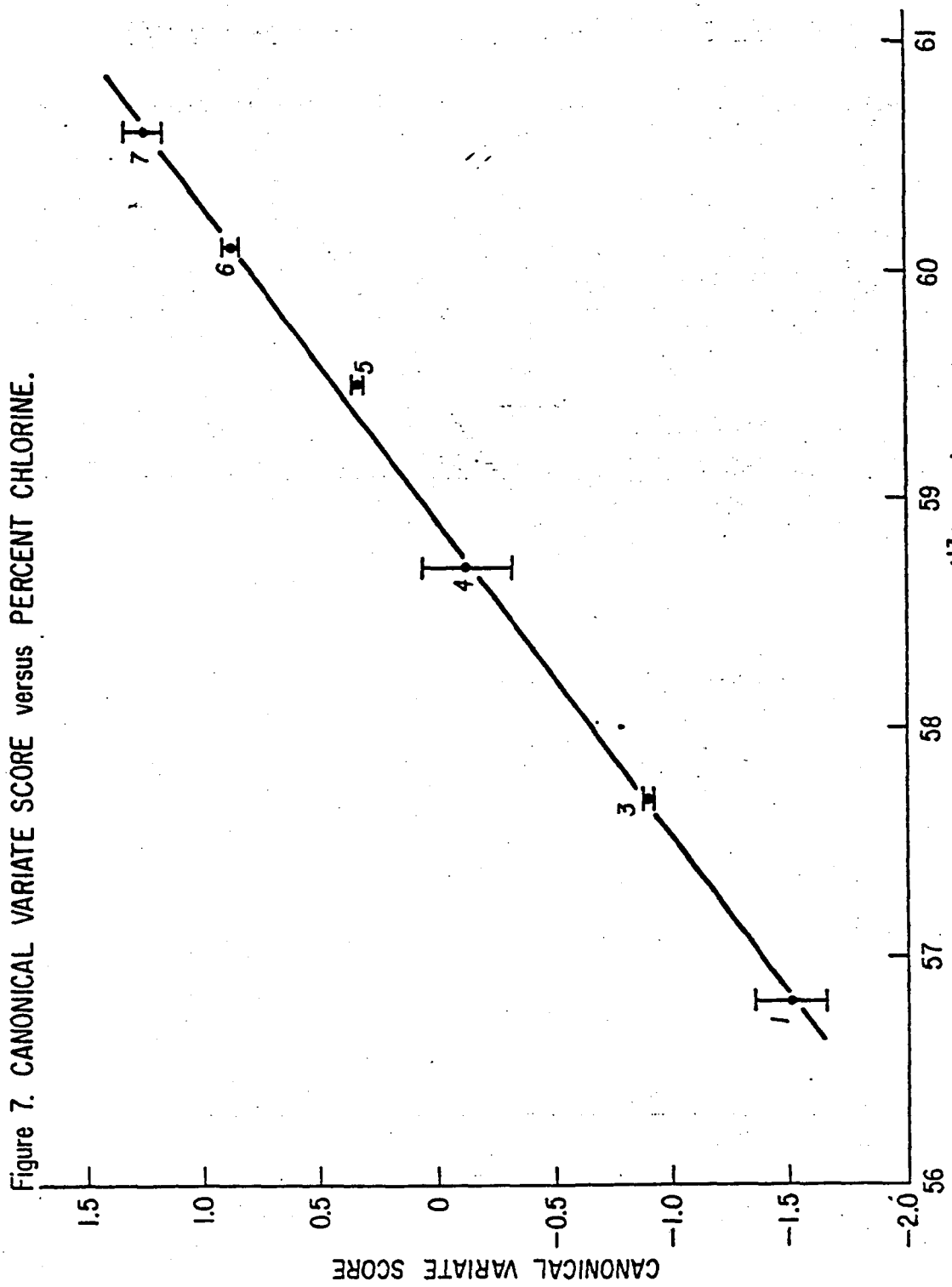


Figure 7. CANONICAL VARIATE SCORE versus PERCENT CHLORINE.

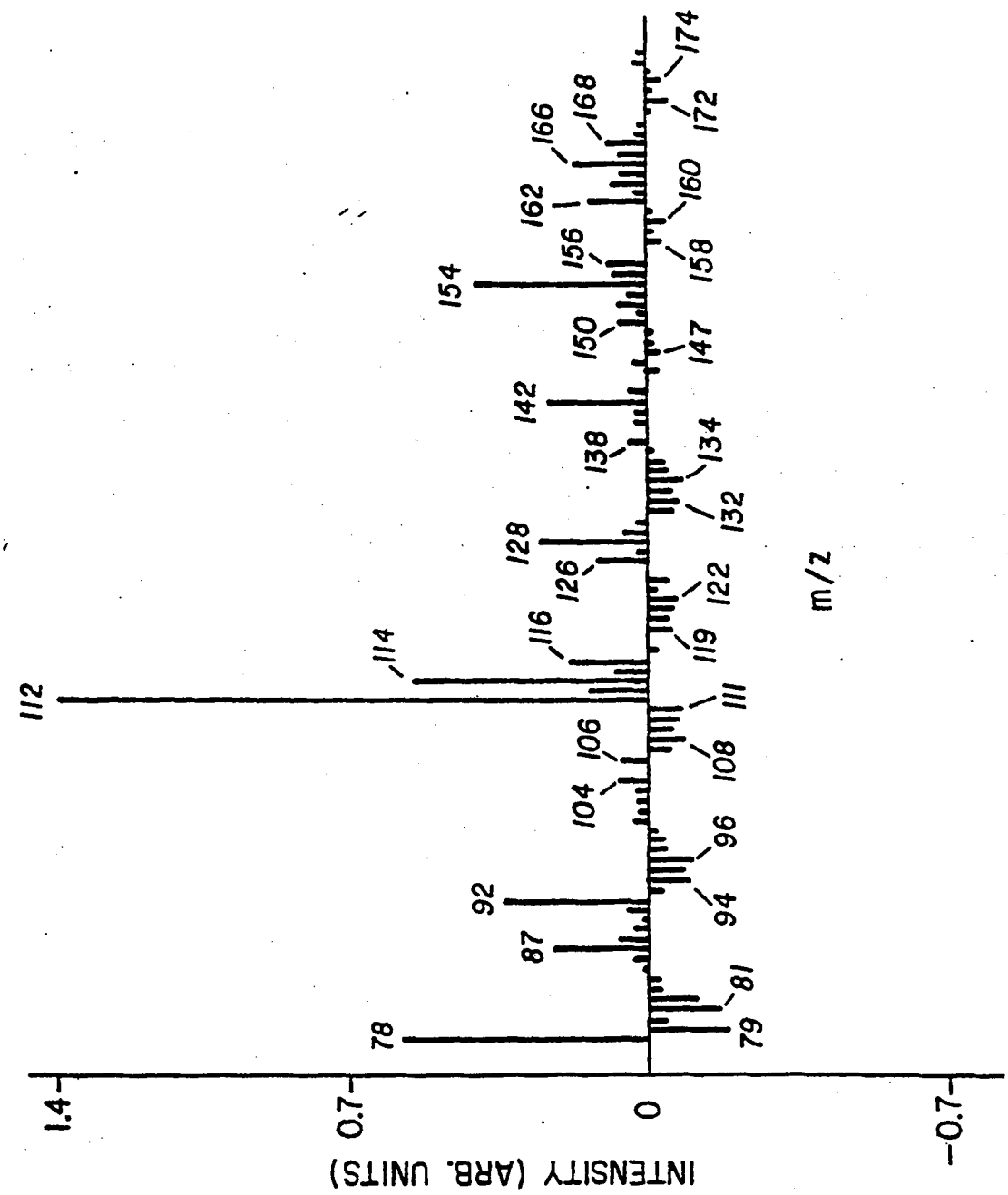


Figure 8. CANONICAL VARIATE SPECTRUM.

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REPORT

BFG CHEMICAL CO.

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J. N. LINDMAY	ALTC/PSC	1/23/84	002-147-101
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R. D. HARDESTY	ALTC/416	4064-0100	

SUBJECT -

MALEIC ANHYDRIDE MONITORING FOR NEW BROWN GEON® COMPOUND

INTRODUCTION-SUMMARY

A new brown Geon® compound is being developed for use as a window frame profile. The stabilizer used, tin bis(butyl maleate) has the potential to generate maleic anhydride during compounding. At various times during this development, mill room operators have experienced headaches as well as eye and respiratory irritations. To determine if maleic anhydride (M.A.) could be the possible cause of those discomforts air samples were monitored during a compounding (1/11-12/84) and an extrusion run (1/18/84). Two out of nine samples submitted for M.A. analysis were over the TLV of 1.0 mg/m³ with the highest levels found at the #6 mill roll (3.38 mg/m³) 1/11/84 and at the Banbury drop pan (40.7 mg/m³) 1/12/84. All further production runs of the brown Geon compound are being temporarily postponed pending future work on [illegible] line which is enclosed and internally ventilated.(1)

[illegible] collected in midget impingers containing [illegible], monitoring pump problems were [illegible] of samples #183 and #76. All [illegible] high performance liquid chroma- [illegible] from NIOSH Procedure PACAM 302.(2) [illegible] was measured and analyzed by the procedure [illegible] are reported as mg/m³.

[illegible] samples analyzed and the results obtained. [illegible] was detected, the minimum detectable [illegible] brackets. These MDL values vary due to [illegible] and air volumes. Samples #2 and #182 [illegible] the TLV of 1.0 mg/m³. The high minimum [illegible] of sample #3 (<3.28) was obtained due to [illegible] low air volume.

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TABLE I

CHROMATOGRAPHIC CONDITIONS USED FOR MALEIC ANHYDRIDE ANALYSIS

Sample:	50 µl of Impinger Solution
Mobile Phase:	0.01 M KH_2PO_4 (pH = 3.0)
Flow Rate:	1.5 mL/min.
Column:	Radial Pak C18
Detection:	UV at 254 nm

TABLE II

RESULTS OF AIR MONITORING FOR MALEIC ANHYDRIDE

		LOCATION	CONCENTRATION (mg/m^3) a
[illegible]	[illegible]	Top Danbury Shaft	0.078
[illegible]	[illegible]	Danbury Drop Pan	(<0.31)
[illegible]	[illegible]	[illegible]	3.38
[illegible]	[illegible]	Top Danbury [illegible]	(<0.85)
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible] the values

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DOCUMENT NUMBER: 20731001

Pulled for Attorney-Client Privilege / Work Product

THE FUNCTION OF MOLYBDENUM ADDITIVES IN THE THERMAL DECOMPOSITION OF POLY(VINYL CHLORIDE)

BY

WILLIAM J. KROENKE
THE BFGOODRICH COMPANY
RESEARCH AND DEVELOPMENT CENTER
BRECKSVILLE, OH

Abstract

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This talk presents the results of recent research studies aimed at determining how molybdenum acts to change the thermal decomposition pattern of PVC. Smoke and char formation during combustion will be related to the products formed during inert atmosphere pyrolysis. Gas chromatography-mass spectrometry-pyrolysis studies were used to characterize the volatile pyrolyzates. Pyrolysis studies were made using heterotactic, perdeuterated, and $^{13}C_2$ PVC compounds.

Synthesis and use of 2,4,6-trichloroheptane as a model compound for PVC provided unexpected insight into the molybdenum promoted PVC decomposition mechanism. Precursors to char were observed for the first time. The results were also inconsistent with the Lewis acid and reductive coupling mechanisms respectively proposed by researchers at Bell Laboratories and BFGoodrich.

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Dr. Geoffrey A. Lindsay	Manager, Corporate Research - Brecksville	
FROM	FIELD POINT OR DEPT. & BLDG. NO.	DATE THIS LETTER
	Research & Development Center- Brecksville	2-15-83

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R. J. Fawcett/d

R. J. Fawcett

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Molybdenum compounds are a versatile class of smoke and fire retarder additives for poly(vinyl chloride), PVC. They act to change the thermal decomposition pathways of PVC. Although PVC is naturally fire retardant, when it is forced to burn, it generates smoke and leaves behind only a small residue. Molybdenum additives, in contrast, significantly reduce smoke formation and promote the formation of char which decreases the amount of PVC available as fuel.

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Synthesis and use of 2,4,6-trichloroheptane as a model compound for PVC provided unexpected insight into the molybdenum promoted PVC decomposition mechanism. Precursors to char were observed for the first time. The results were also inconsistent with the Lewis acid and reductive coupling mechanisms respectively proposed by Starnes and Edelson[3] and Lattimer and Kroenke.[10]

INTRODUCTION

Fire safety is a universal concern. As outlined in a recent feature article in Chemical and Engineering News,[1] there is no universal agreement on the relative fire hazards of natural materials compared to synthetic materials. During combustion, both of these materials form smoke and toxic gases. The essential question, which remains unanswered, is whether the increased use of synthetic materials is resulting in an increased fire hazard?

The issues are very complex. While it is unanimously agreed that carbon monoxide is the number one toxic gas hazard in the combustion of most materials, natural or synthetic, the role of other toxic gases specific to certain materials is much less clear, and is surrounded by controversy.

The situation with regard to smoke is better understood and much less controversial. Smoke obscures vision and impairs a persons ability to flee a fire situation. This obscuration of vision tends to promote hysteria, which in turn results in misorientation and panic. While smoke is a product of most combustion processes and large scale fires, under similar laboratory test conditions some synthetic materials generate more smoke than wood. However, the ranking of materials in terms of smoke generation is very dependent on the specific test conditions. For example, under smoldering conditions, wood burns with the generation of copius quantities of smoke. In contrast, it generates little smoke under flaming conditions where it burns with a rapid flame spread.

PVC behaves just the opposite of wood. When it is forced to burn, it generates little smoke under smoldering conditions, but significant smoke under flaming conditions. However, even in the flaming mode, it has a rate of flame spread significantly less than that of wood.

The objective of the research reported here was to further reduce the already low flammability and combustibility properties of PVC. Special emphasis was placed on reducing the smoke generated from PVC when it is forced to burn, and in reducing its toxic gas hazard by reducing the amount of PVC which behaves as, or generates, a fuel for combustion. The approach selected was to find chemistries which would alter the normal thermal degradation pathways of PVC and promote the formation of a thermally stable char.

The first part of this talk concerns the thermal decomposition pathways of PVC. New mechanisms for the formation of volatile aromatic pyrolyzates will be presented. These are consistent with the results from deuterium and ^{13}C labeling studies. In the second part of this talk the development of appropriate smoke and fire retarder systems for PVC will be discussed. Particular emphasis will be placed on identifying the most effective additive systems, and the problems involved in developing smoke and fire retarder systems for commercially useful PVC compounds.

The third part of this talk deals with the role of the metal-based smoke and fire retarders in reducing the formation of smoke and promoting the formation of char. Molybdenum based smoke and fire retarder additives will be featured. More specifically, the discussion will center around the mechanism(s) by which molybdenum trioxide (MoO_3) acts as a smoke and fire retarder for PVC. The results of pyrolysis, gas chromatography, mass spectroscopy (PY-GC-MS) experiments performed on a wide variety of different PVC compounds will be discussed.

EXPERIMENTAL

The model rigid PVC compound is 100 parts Geon® 103EP resin, 2 parts microthene 510 polyethylene, and 2 parts dibutyltin bis(isooctylthioglycolate). The Geon® resin is a homopolymer with an inherent viscosity of 0.98-1.04 and an ASTM classification of GP-5-1443. The microthene 510 is a processing aid while the tin thioglycolate is a stabilizer.

The PVC samples containing the candidate smoke retarders were prepared by milling at about 160°C on a rolling rubber mill. Sheets of appropriate thickness were molded under pressure at about 165°C.

Smoke evolution primarily was determined by means of the NBS Smoke Chamber test. The PVC samples measured 7.3x7.3x0.06 cm and were burned in the flaming mode in accordance with ASTM-E-662-79 "Test for Specific Optical Density of Smoke Generated by Solid Materials". In this article, the NBS smoke number is expressed as D_m/g which is the smoke generated per gram of sample.

In certain cases, smoke evolution was determined by both the NBS Smoke Chamber test and the Goodrich Smoke-Char test. The char-forming characteristics of certain of the polymer samples also were determined using the Goodrich Smoke-Char test.

This smoke-char test is a small scale laboratory test which is useful for quickly evaluating the smoke-forming and char-forming characteristics of polymer samples. Small (0.3-0.4 gm) polymer samples measuring about 1.3x0.95x0.19 cm are placed on a screen and forced to burn by being totally immersed in the flame from a propane torch (276 Pa) for 1 min. The smoke from the burning samples rises through a vertical chimney and passes through the beam of a photometer. The photometer is coupled with an integrator which provides a measure of the total smoke evolved. The smoke number, SPVC, is expressed as integrated area per gram of PVC in the polymer sample.

The residue of "char" remaining after the smoke-char test is weighed and used to calculate the "percent of backbone char" (% BC). Essentially, % BC represents the amount of the PVC hydrocarbon backbone which has been retained as a thermally stable char. It is calculated as shown:

$$\% \text{ BC} = \frac{\text{char wt - nonburnable residue wt}}{\text{sample wt - non-PVC weight - HCl wt}} \times 100$$

A CDS model 100 Pyroprobe was used. Platinum ribbon or coil probes were used when appropriate. Typical pyrolyses were carried out for 20-30 sec at 550-600°C; the Pyroprobe temperature had been calibrated by CDS (optical pyrometer). The pyrolyses were conducted in dry helium environment at a flow rate of ~30 cm^2/min. Polymer samples were deposited on the ribbon via syringe from tetrahydrofuran solution. The solvent was allowed to evaporate in air before pyrolysis was carried out.

The pyrolyzates were analyzed by gas chromatography/mass spectroscopy. The GC/MS system consisted of a Varian 3700 Digital gas chromatograph, a Varian MAT (now Finnigan MAT) 311A mass spectrometer, and a Finnigan ENCOS 2400 data system. Typical system temperatures were as follows: PY-GC interface (injector), 150°C; GC-MS interface, 290°C; ion source, 220°C. Pyrolyzates were separated on a 4 m x 2 mm ID glass 3% Dexsil 300 on 100/120-mesh Supelcoport column, programmed from 50-250°C at 15 deg/min after a 2-min hold on injection.

Most of the PY-GC-MS runs were made in EI mode (~38 eV) using a combination chemical ionization/electron impact ion source. For the

cooled in dry ice. The $^{13}C_2$-VCM was added by injection the gas under the surface of the cold liquid. Using a Pyrex capillary, nitrogen was bubbled slowly through the mixture. After one minute, the tube was sealed with a torch. The nitrogen purge was continued until the flame collapsed the capillary.

The sealed tube was tumbled for 16 h at 50°C. The tan, waxy product was dissolved in tetrahydrofuran and precipitated with methanol. Yield of polymer was 59 mg (15%). A control sample was prepared under the same conditions using $^{12}C_2$-VCM; the yield of polymer (a white powder) was 62%.

VOLATILE AROMATIC PYROLYZATE FORMATION FROM POLY(VINYL CHLORIDE)

Introduction

A fundamental goal in this study was to determine the basic mechanisms by which volatile aromatic pyrolyzates form from PVC in the absence of additives. As will be shown in a latter section of this talk, the combustion of aromatic pyrolyzates is the principle source of smoke from burning PVC. Furthermore, the effect of smoke retarders we have developed for PVC are known to interfere with the normal mechanisms by which volatile pyrolyzates form. Thus we hoped a good understanding of pyrolysis mechanisms in virgin PVC would provide insight into the mechanisms by which smoke-reducing and char-forming additives work in PVC compounds.

Our earlier PY-GC-MS studies in this area used GC-field ionization mass spectroscopy (FI-MS) to analyze the volatile pyrolyzates.[2] The use of FI-MS greatly simplified the spectral interpretation in deuterium tracer experiments, since essentially the only ions observed were molecular ions. Unfortunately, however, GC-FI-MS is not a very sensitive technique compared to GC-electron impact mass spectroscopy (EI-MS). In the first studies, we used relatively large quantities of PVC (~2 mg) in the pyroprobe in order to obtain sufficient amounts of pyrolyzate for adequate FI-MS detection. However, we found that secondary pyrolysis reactions were enhanced by the relatively large quantities of PVC and gave more H/D mixing than would be expected from primary pyrolyzate formation mechanisms.

The use of EI/MS at normal electron energies (~70 eV) gives optimal sensitivity for detection. However, when a mixture of isotopic species is present, fragmentation reactions lead to very complex mass spectra that are difficult to interpret. For example, in our first pyrolysis studies of mixtures of PVC and pedeutero-PVC (DPVC), all isotopic species of toluene from $C_7H_8D_0$ to $C_7H_0D_8$ were observed. An alternative method of analysis, which provides a compromise between FI-MS and 70-eV EI-MS, is lowered voltage EI-MS. At lowered voltage the sensitivity for detection is intermediate between EI-MS and FI-MS. The mass spectra are simpler than 70-eV EI spectra but more complex than the simple molecular ion FI spectra.

In this work we have repeated our PY-GC-MS experiments with intimate mixtures of PVC and DPVC using smaller quantities of polymer in the pyroprobe (~40 μg compared to ~2 mg). The pyrolyzates were analyzed by

steps.[4] The cyclohexadiene intermediate (II) seems reasonable based on consideration of activation energies.[5] The conversion of II to III is likely a two step process, since a concerted reaction is not allowed by orbital symmetry.[3] Also, the presence of macroradical intermediates during PVC decomposition has been verified by ESR experiments.[6] Finally, the calculated activation energies for conversion of II to III via a two-step process seem consistent with the observed elimination of benzene at relatively low temperatures.

Toluene Formation

Two distinctly intermolecular pathways for toluene formation are depicted in Figure 3. Scission of the cyclohexadiene intermediate (VI) via pathway A leads to intermediate VII. Another chain scission followed by H/D abstraction from an adjacent chain leads to toluene (VIII) in which one hydrogen atom originates from an intermolecular reaction. Alternatively, pathway V leads to an intermediate (IX) containing a benzylic chloride. Chlorine replacement by H/D leads to intermediate X. Subsequent chain scission and H/D addition leads to toluene (XI) in which two hydrogen atoms originate from intermolecular reactions. Note in Figure 3 that the two key stable intermediates, VII and X, can "preform" in the polymer during the early stages of pyrolysis (i.e., during dehydrochlorination). There is some experimental evidence for the formation of these types of "benzenoid" structures in partially degraded PVC. If one makes the assumption that each pathway has approximately equal probability, predictions can be made as to the expected isotopic abundances of the toluene product. We will assume a primary kinetic isotope affect (k_CH/k_CD) of 2.0 which is reasonable for a high temperature reaction (~600°C). The results of the predictions (Figure 4) show rather good agreement with the actual isotopic abundances (Table 1). The most abundant species are C_7H_8 and C_7HD_7. This agreement suggests that Figure 3 and the above assumptions may be quite reasonable. Also note that it was unnecessary to invoke crosslinking reactions (intermolecular C-C bond formation) as a route to transfer H/D.

An alternative to Figure 3 would be the formation of intermediates in which methyl groups attached to cyclohexadiene rings are "preformed" in the earlier stages of polymer decomposition from the cyclohexadiene intermediate (VI). However, the kinetic isotope effect predictions (Figure 4) would be the same.

Formation of Other Aromatic Pyrolyzates

Two pathways are possible for styrene. One is completely intramolecular and requires no intermolecular H/D mixing. The other requires one intermolecular H/D transfer. Using the same type of analysis scheme as used for toluene results in a predicted isotope distribution in reasonably good agreement with the experimental values.

The indene analysis parallels that of styrene; one intramolecular pathway and one requiring an intermolecular H/D transfer. Again, the agreement between experiment and prediction is reasonable. Naphthalene, like benzene, forms mainly from intramolecular pathways. A formation

mainly related to changes in the environment around the molybdenum ion. Some comments about particle size and dispersion characteristics, however, are in order. Although MoO_3 is the most effective compound, it and ammonium dimolybdate have the poorest dispersion characteristics. Grinding the ammonium dimolybdate to reduce its average particle size improved its performance, so it behaved much like the ammonium octamolybdate. In contrast, while grinding improved the dispersion characteristics of the MoO_3, it did not improve its performance. In addition, commercially available samples of molybdenum trioxide, designed to have higher surface areas and smaller particle sizes gave the same level of performance.

We decided to emphasize the development of molybdenum compounds as fire and smoke retarder additives. Because many of them are quite effective, white, and in small scale laboratory studies process reasonably well into PVC. In particular, we decided to place our initial emphasis on molybdenum trioxide, MoO_3, because it is the least expensive and most readily available molybdenum compound, and because it has a very favorable smoke reduction-concentration effect. Figure 9 illustrates that increasing the loading of MoO_3 from 2 to 10 phr continually reduces smoke formation. It must be mentioned again that such relationships only hold over a limited range of concentration. For example, in the case of MoO_3, the concentration-loading curve normally plateaus out around 10 phr. So additional MoO_3 above this level will provide relatively small improvements in performance. Other potentially interesting molybdenum compounds such as ammonium dimolybdate exhibited a very flat smoke-concentration relationship (Figure 10).

Smoke Reduction and Char Formation

The relationship between smoke and char is critical in understanding the role of MoO_3 and other metal smoke retarders in PVC. All of the effective smoke retarders we have studied effectively act to promote the formation of char while they decrease the formation of smoke. The smoke-char relationship is illustrated for a variety of metal smoke retarders in Tables 5 and 6. As is illustrated, MoO_3 is one of the most effective char formers. Essentially all of the effective metal based smoke retarders studied appear to work in the solid state, not in the vapor state. While the possibility that some of the retarders provide a vapor phase activity cannot be ruled out, their main function appears to be that of interfering with the normal thermal degradation pattern of the PVC. The most visible manifestation of this solid state activity is the formation of char. All of the effective smoke retarders reported here promoted the formation of char. Char yields of 30-50% BC are typical. This compares to % BC of about 10 for the rigid control compound (Table 4). However, in a series of closely related smoke retarders or retarders used at different loading levels, there may be a non-regular relationship between smoke reduction and char formation. For example, in such a series, the compound giving the lowest smoke may not always form the most char. But using the Goodrich Smoke-Char test and the flaming mode of the NBS Smoke Chamber, even in these cases, smoke reduction is accompanied by char formation.

cyclization to form benzene, are stable to higher temperatures where different mechanisms ensue to give aliphatic (less smoky) products.

The Bell reports considered two possibilities for trans polyene formation. One is the straightforward Lewis acid isomerization of cis alkenes into trans alkenes. The other has the MoO_3 acting as a Lewis acid which interacts with chain chlorines and induces dehydrochlorination. If a dissociated ion pair forms without retention of the original stereochemistry, trans polyenes can be formed directly during dehydrochlorination.

We did not believe the "cis-trans" Lewis acid mechanism as originally proposed by Bell Laboratories' workers[9] explains the primary role of MoO_3 as a smoke retarder in PVC. It is weak in several respects, both on its own merits and also with regard to the results presented here and in previous work.[8]

Our most serious objection to the "cis-trans" Lewis acid theory is with regard to its predictions of volatile pyrolyzate formation. Lewis acids can promote the isomerization of both cis and trans double bonds; the trans configuration is thermodynamically more stable. Even if trans polyenes are formed initially upon dehydrochlorination, we would expect rapid cis-trans interconversion to occur at the high temperatures and enthalpies encountered in later stages of PVC thermal decomposition. This might lead, for example, to enhanced evolution of benzene at higher temperatures, yet the evidence does not show this. The Lewis acid theory also predicts that aliphatic products will be formed from polyene chains in preference to aromatics. The theory predicts that these aliphatics will burn cleanly (with little smoke). These compounds, however, will in general be unsaturated since they are derived from polyene chains. Thus, they should burn with a smoky flame, similar to benzene and other aromatics.

In fairness to the Bell workers, in their detailed discussion of the Lewis acid mechanism, they do point out that in addition to cis-trans effects, MoO_3 or species derived from it might destroy the olefinic precursors of benzene by catalyzing intermolecular Diels-Alder cycylizations or Friedel-Crafts alkylations. This would lead to crosslinking of the thermally decomposing PVC chains segments. However, they state that completely convincing correlations of char yield with smoke emission or Lewis acid content have not been observed in published combustion studies. And they conclude "that crosslinking catalyzed by metal species has not been established as the principle mechanism for smoke inhibition, although it undoubtedly occurs in many systems".

Our mechanistic studies were undertaken with two thoughts in mind. One was to test the Lewis acid mechanism, the other was to search for alternate explanations consistent with our experimental results and the published results of other workers.

Smoke and Char Formation

The model PVC compounds (with and without MoO_3) were examined in the flaming mode of the NBS smoke chamber, and also in the Goodrich Smoke-

tic PVC (SYN), (3) 100 parts PVC plus 10 parts MoO_3, and (4) 100 parts SYN plus 10 parts MoO_3. Pyrolyses were carried out in a helium atmosphere at 550°C for 20 sec. Quantitative determinations for benzene and toluene pyrolyzates were made on each sample. Response factors were determined (external standard method) by injection of standard solutions of benzene and toluene (n-pentane solvent; porapak PSGC column). The syndiotactic PVC sample was prepared by a urea complexation method and was reported to be nearly 100% syndiotactic. Samples 3 and 4 were mixed with an agate mortar and pestle. The results are reported in Table 9. Instead of the expected 50% or better reduction in benzene relative to the controlled PVC sample, only a 25% reduction was observed. Also, if the principle action of the smoke retarder is to induce the formation of trans polyene segments on dehydrochlorination, one would expect the metal additive to have less effect in syndiotactic PVC than in "normal" 103EP-F76. In fact, MoO_3 reduced benzene by only approximately 57% in 103EP-F76 compared to approximately 72% in syndiotactic PVC. The MoO_3 smoke retarder also is effective in reducing toluene formation, but the 40-50% reduction is smaller than for benzene. We conclude that MoO_3 must be doing more than acting as a Lewis acid isomerization catalyst.

Perdeutero-PVC Pyrolysis Results

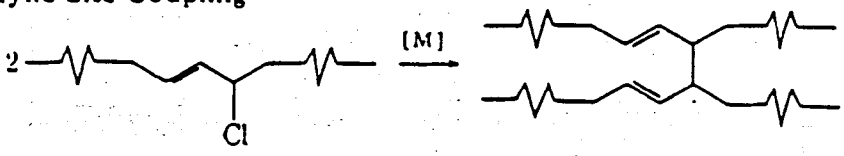
Two PVC samples were used. The "normal" PVC sample was Geon 103EP-F76 prepared by suspension polymerization at 50°C. (This was the same PVC sample used for the smoke, char, and volatile pyrolyzate tests.) The perdeutero-PVC samples (DPVC) was prepared by the suspension polymerization of C_2D_3Cl (reported deuterium enrichment 97.3%) at 50°C. GPC-derived parameters were $\bar{M}_n = 1.9 \times 10^5$ and $\bar{M}_w = 3.9 \times 10^5$.

Deuterium enrichment experiments were conducted with the following simple compounds: (1) PVC/DPVC (coprecipitate) and (2) 100 parts PVC/DPVC plus 10 parts MoO_3. Pyrolyses were carried out in helium atmosphere at 550°C for twenty seconds and deuterium enrichments for selected pyrolyzates were calculated from the field ionization mass spectral data. In each experiment the polymer sample used was an equal weight coprecipitate of PVC (103EP-F76) and DPVC. The PVC/DPVC coprecipitate and MoO_3 were mixed with an agate mortar and pestle. About 2 mg of sample was pyrolyzed in each run; duplicate runs were made on both Dexsil 300 and Poropak PS-GC columns.

The isotopic distributions for selected pyrolyzates are listed in Table 10. Corrections have been made for natural abundance of ^{13}C. No corrections for molecular ion fragmentation were necessary, since pure molecular ion spectra were obtained by field ionization. All pyrolyzates listed, excepted for benzene, showed very extensive H/D mixing in the MoO_3 compound. Benzene gave relatively little H/D mixing indicating that benzene must be formed intramolecularly even with the smoke retarder present. The total amount of benzene formed with the smoke retarder was, of course, greatly reduced (see Tables 8 and 9).

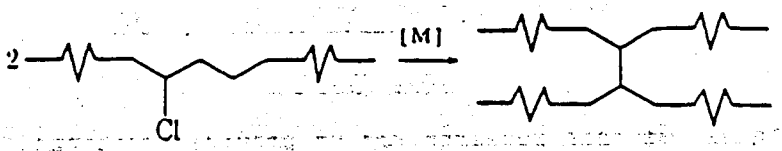
With MoO_3 present, naphthalene and the other aromatic pyrolyzates containing alkyl groups all showed considerable H/D mixing. Their formation must involve intermolecular reactions. Such intermolecular reactions could be crosslinking of the decomposing polymer chains follow-

(a) Allylic Site Coupling



(1)

(b) Alkyl Site Coupling



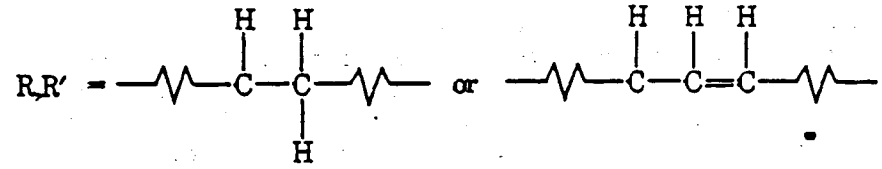
(2)

Reductive coupling reactions are quite common in organometallic chemistry. Interestingly, the reaction sequences seem best established for copper compounds, the most effective class of smoke retarders for PVC. With copper as the metal, 1,1 elimination (or "cross-coupling") may be a feasible pathway to effect reductive coupling. This involves a single cation and can be formalized as follows:

$$R\cdot + Cu^0 \rightarrow R{-}Cu^I \quad (3)$$

$$RCu^I + R' - Cl \rightarrow [RR'Cu^{III}Cl] \quad (4)$$

$$[RR'Cu^{III}Cl] \longrightarrow R{-}R' + Cu^ICl \quad (5)$$

where R,R' =  or

This pathway involves two oxidative additions, reactions 3 and 4, followed by the reductive elimination, reaction 5, to give the coupled product (R-R'). An alternate means of forming the Cu^{III} intermediate would be the oxidative addition of two radicals (R· and R'·) to Cu^ICl. The initiating radical can be formed via PVC chain scission reactions or else via chlorine extraction by the metal additive.[2,3]

$$R - Cl + Cu^0 \rightarrow R\cdot + Cu^ICl \quad (6)$$

Although we felt less confident about postulating a "reductive coupling" scheme based on low valence molybdenum species, we proposed a mechanism based on a dinuclear transition state exhibiting Mo-Mo bonding.

$$R - Cl + Mo^n \rightarrow [R - Mo^{n+2} - Cl] \leftarrow Mo^{n+1} - Cl + R\cdot \quad (7)$$

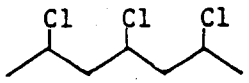
$$2[Cl - Mo^{n+2} - R] \rightarrow \left[\begin{array}{l}\text{Dinuclear}\\ \text{Transition}\\ \text{State(s)}\end{array}\right] \rightarrow R - R + 2Mo^{n+1} - Cl \quad (8)$$

Our secondary criticism of the Bell model compound studies is the low temperatures used. Most of their reactions were carried out between 100 and 200°C. These are unrealistically low thermal degradation temperatures for smoke retarded PVC. From about 17 experiments, only 2 were conducted at temperatures as high as 300°C.

Our final criticism of the Bell model compound studies concerns their failure to adequately report the details (techniques, equipment, procedures) of their experiments. They do not provide sufficient information to enable other researchers to duplicate their experiments and check their results.

2,4,6-Trichloroheptane Model Compound

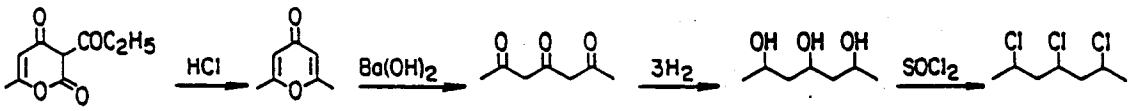
Our model compound is a well-recognized model for PVC -- 2,4,6-trichloroheptane:



In contrast to the model compounds used by the Bell workers, trichloroheptane can "unzip" during pyrolysis to form a polyene chain with three double bonds. This chain can then intramolecularly cyclize to form an aromatic ring. Crosslink formation between adjacent chains also can provide a pathway for forming condensed ring aromatic compounds.

Pyrolysis

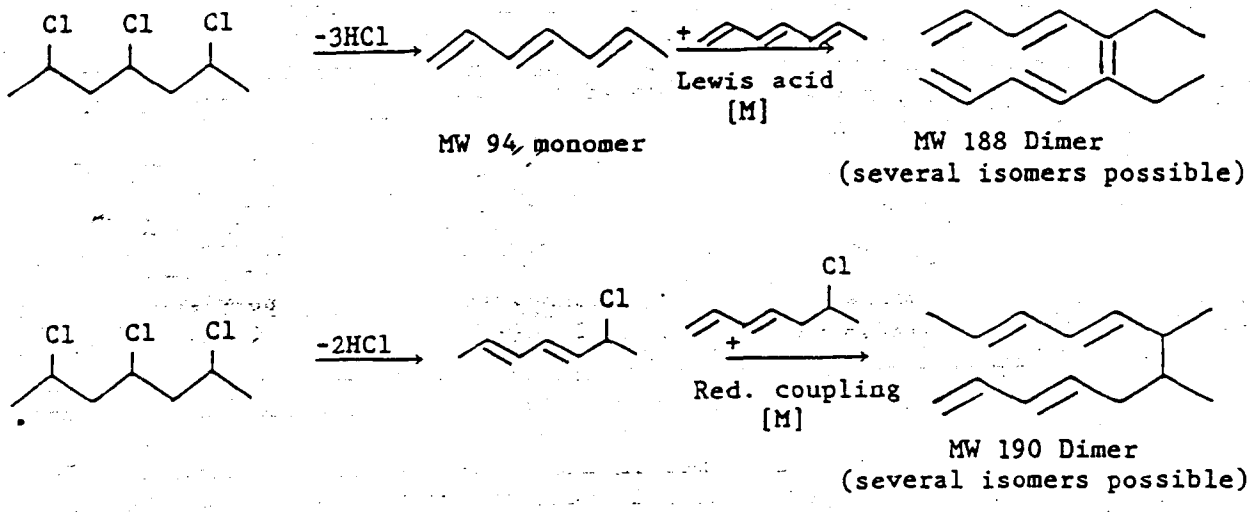
The pyrolyses were conducted in glass capillary tubes which were purged with nitrogen and sealed. Smoke retarders were either dissolved in the 2,4,6-trichloroheptane prior to charging, or uniformly coated on the walls of the capillary tubes. The synthesis of 2,4,6-trichloroheptane used in this paper involved four steps starting with dehydroacetic acid.



The first step involves the acetic rearrangement of dehydroacetic acid. In the second step the 2,6-dimethyl-4-pyrone is ring-opened with barium hydroxide.

The third step, hydrogenation, must be done soon after the second step because the 2,4,6-heptanetrione does not have a very long shelf life. It enolizes very easily and this reduces the yield in step 3, which uses a ruthenium catalyst. Step 4, the reaction with thionyl chloride, is a standard procedure for the conversion of alcohols to chlorides. The final product was distilled twice to separate it from undesired side-products from the chlorination reaction which had similar boiling points.

SCHEME I



Dihydro-oligomers were also detected in the FD-MS analysis of the decomposition products. The field desorption results are listed in Table 14. Since copper compounds are among the most effective catalysts for promoting reductive coupling type reactions, it is reasonable to suggest that the dihydro-oligomers formed via this pathway.

The Molybdenum Trioxide Experiment

This was the most interesting experiment since it gave unexpected results. The first surpise was the formation of a considerable quantity of low-boiling components. Significant low-boils were not formed in the control and copper catalyzed experiments. Headspace analysis, in which the pyrolysis tube was placed in a sealed sample file and subsequently broken, enabled the low-boils to be sampled and analyzed by GC-MS. The following low-boiling components were detected:

A) C_1-C_7 saturated (or alicyclic) hydrocarbons, either straight chain or methyl-branched.

B) C_1-C_7 chlorinated, saturated hydrocarbons.

C) Toluene.

GC-MS and direct probe MS were used to identify the higher-boiling components. The capillary gas chromatogram of the high-boils was very "messy" and contained a large number of isomers for most of the observed species. A listing of the most prominent components is provided in Table 15. The dominant products were alkyl-substituted benzenes and naphthalenes, although some of the normal dimer and its dihydro derivative also were observed. In addition to the products listed in Table 15, there were many more products of higher molecular weight; these were detected using direct probe electron impact MS. The results of the direct probe analysis are summarized in Table 16. The trend established in the results shown in Table 15 continues. Clearly a primary role of

Experimental assistance from Edgar R. Harris, Ilmars Sockis, and Betty A. Starkey is gratefully acknowledged. Helpful support and suggestions were provided by E. Douglas Dickens, Jr., Arthur W. McRowe, and Paul P. Nicholas.

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FIGURE 2

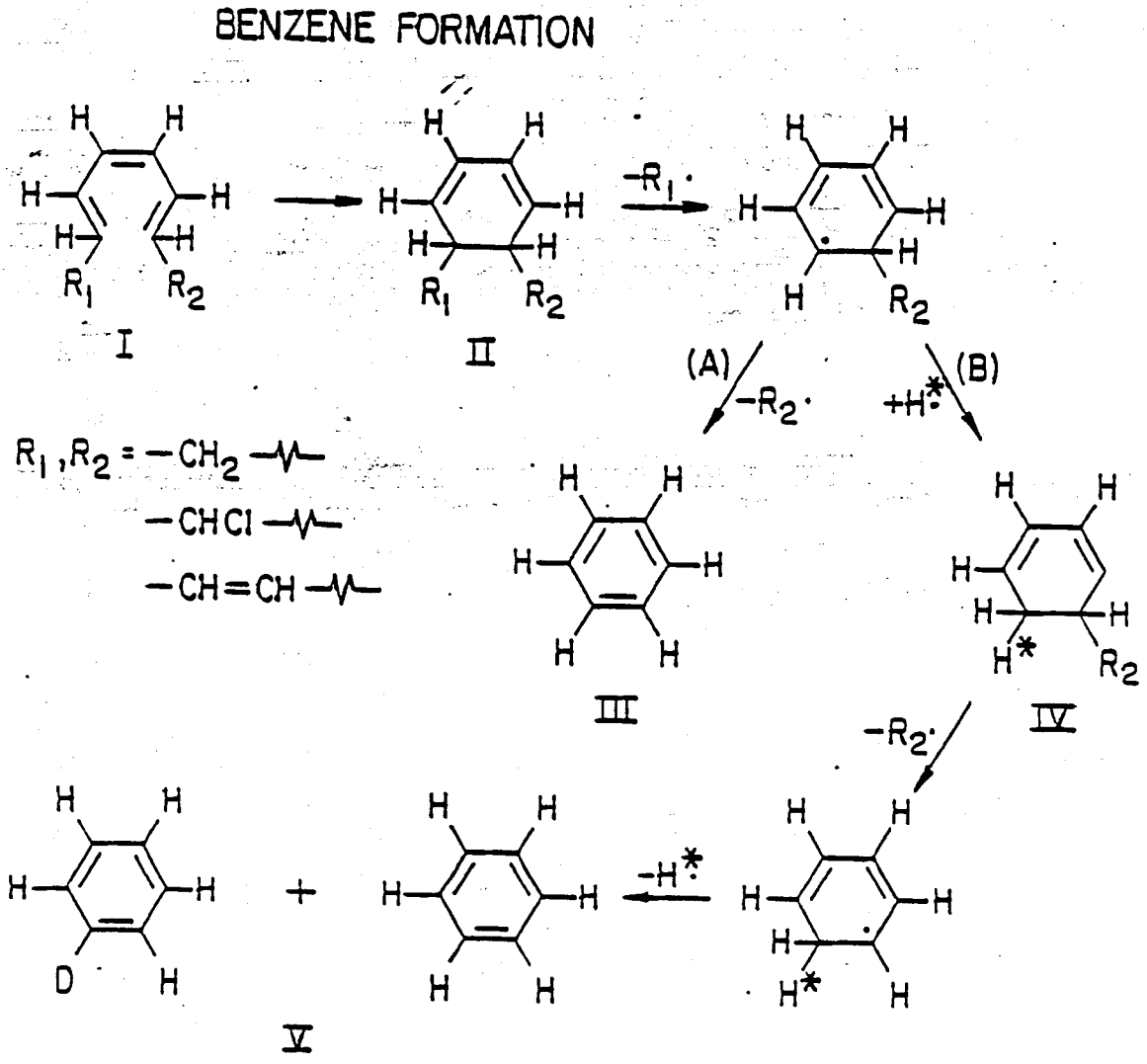
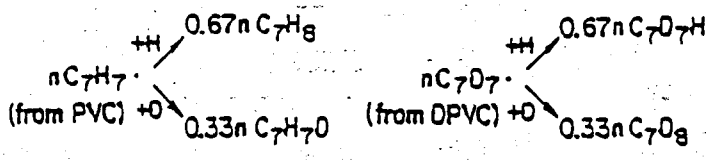


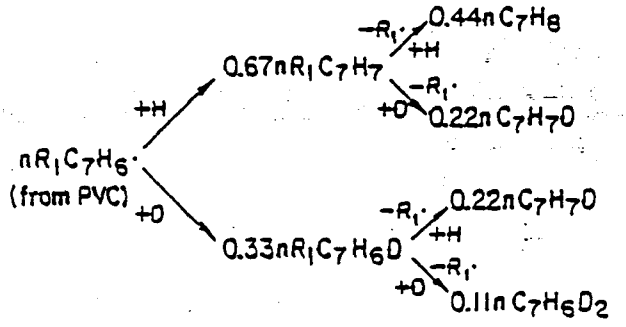
FIGURE 4

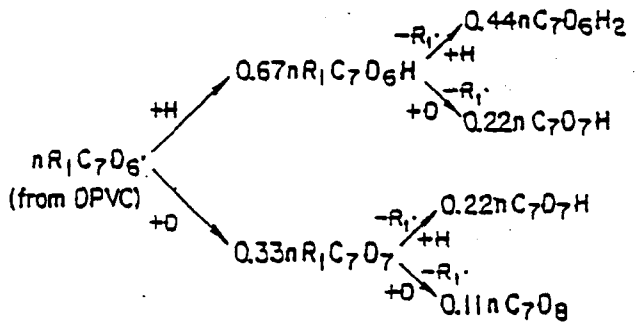
PREDICTED ISOTOPIC ABUNDANCES for TOLUENE

PATHWAY A, SCHEME II



PATHWAY B, SCHEME II





SUMMATION of the VARIOUS PATHWAYS:

	C_7H_8	C_7H_7O	$C_7H_6O_2$	$C_7H_5O_3$	$C_7H_4O_4$	$C_7H_3O_5$	$C_7H_2O_6$	C_7HO_7	C_7O_8
TOTAL	1.11n	0.78n	0.11n	0	0	0	0.44n	1.11n	0.44n
PERCENT	28	19	3	0	0	0	11	28	11

FIGURE 6

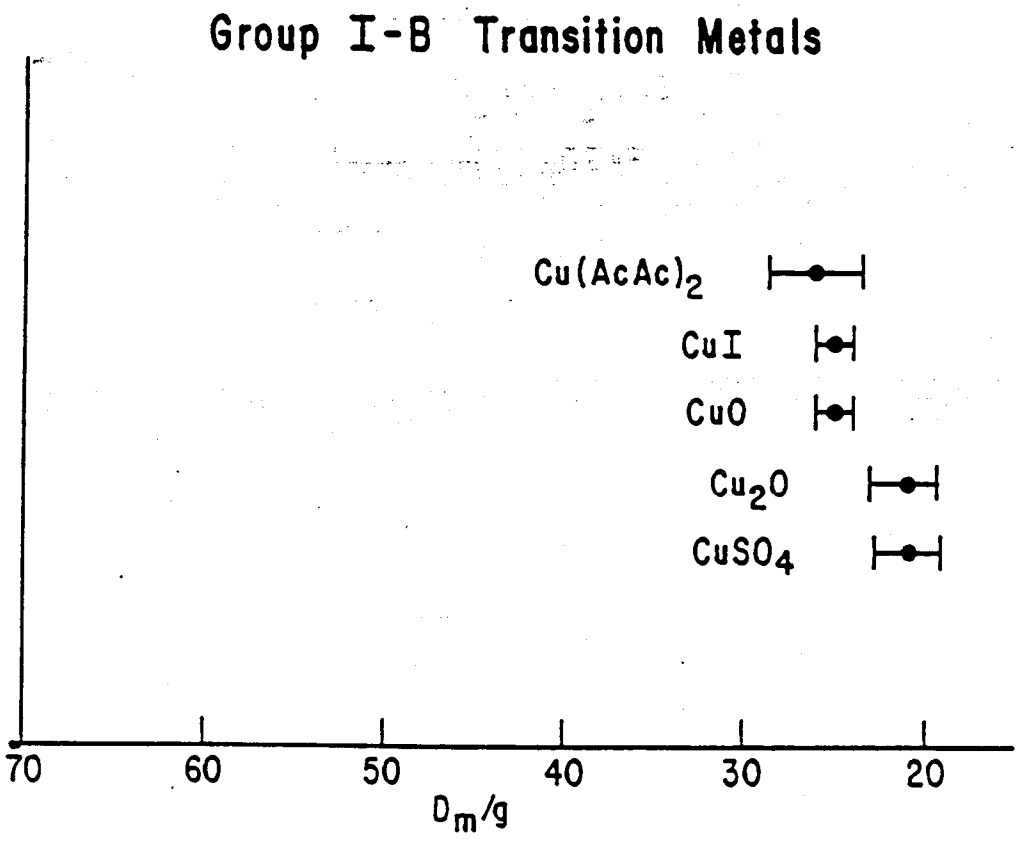


FIGURE 8

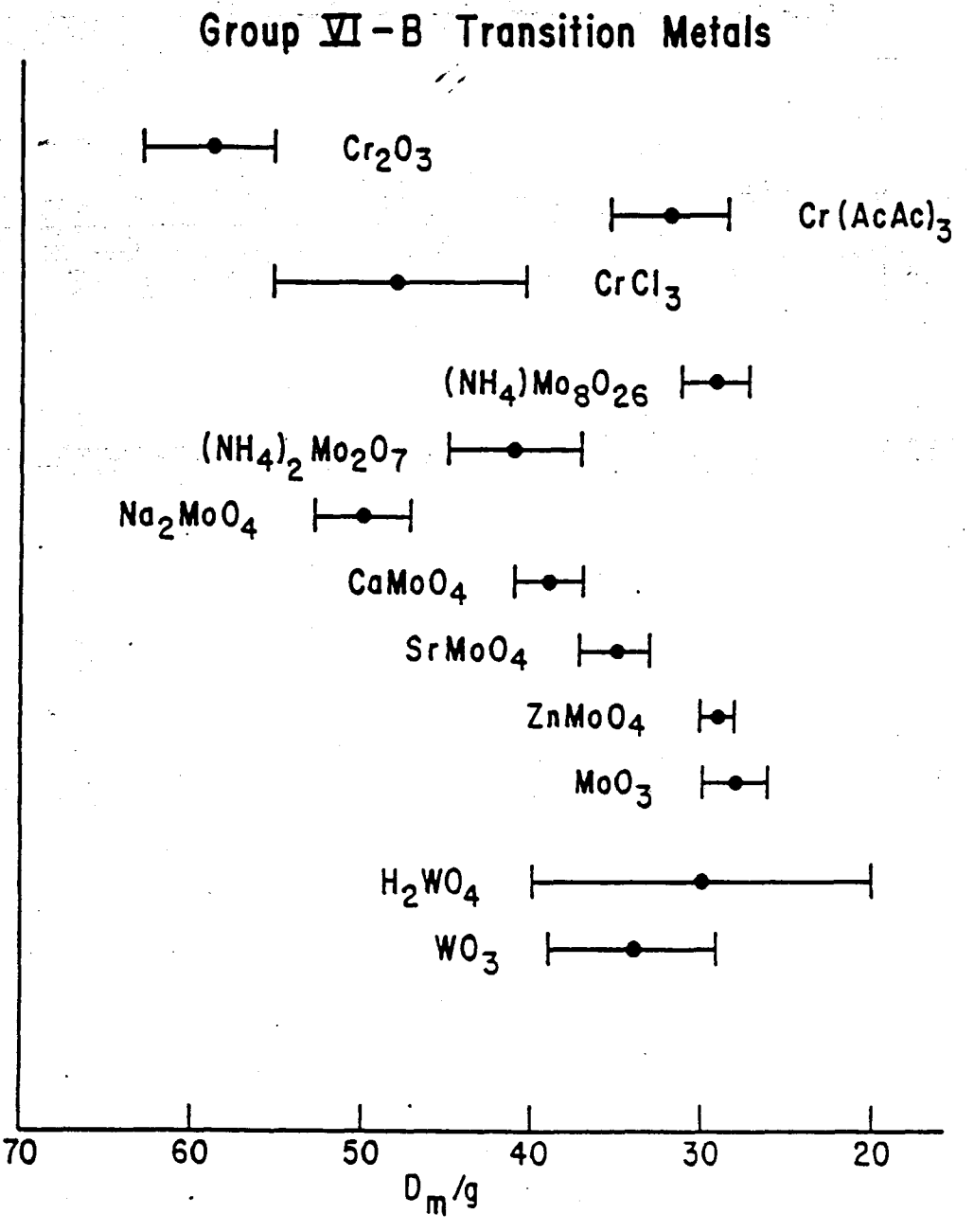


FIGURE 10

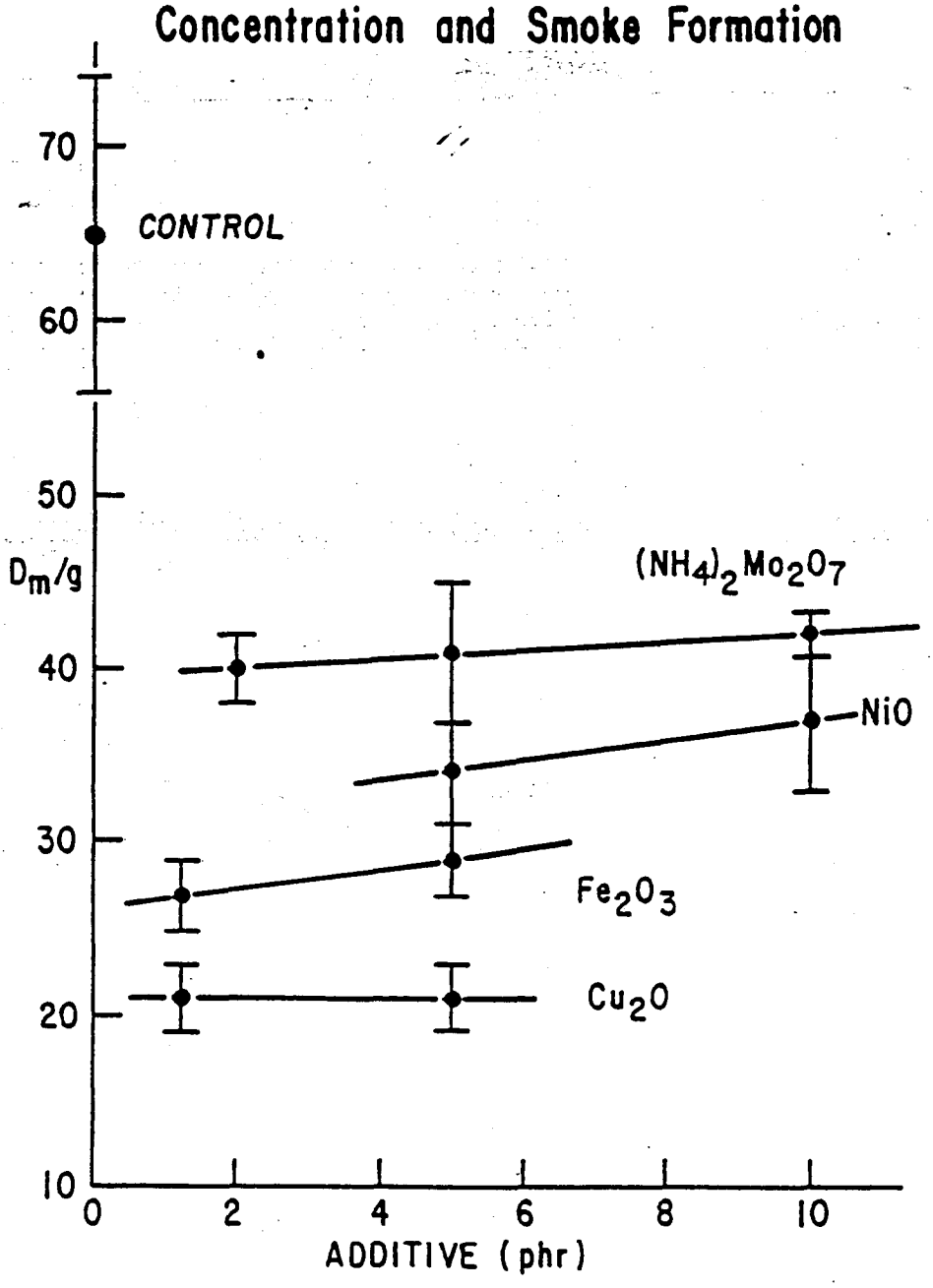


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FIGURE 12

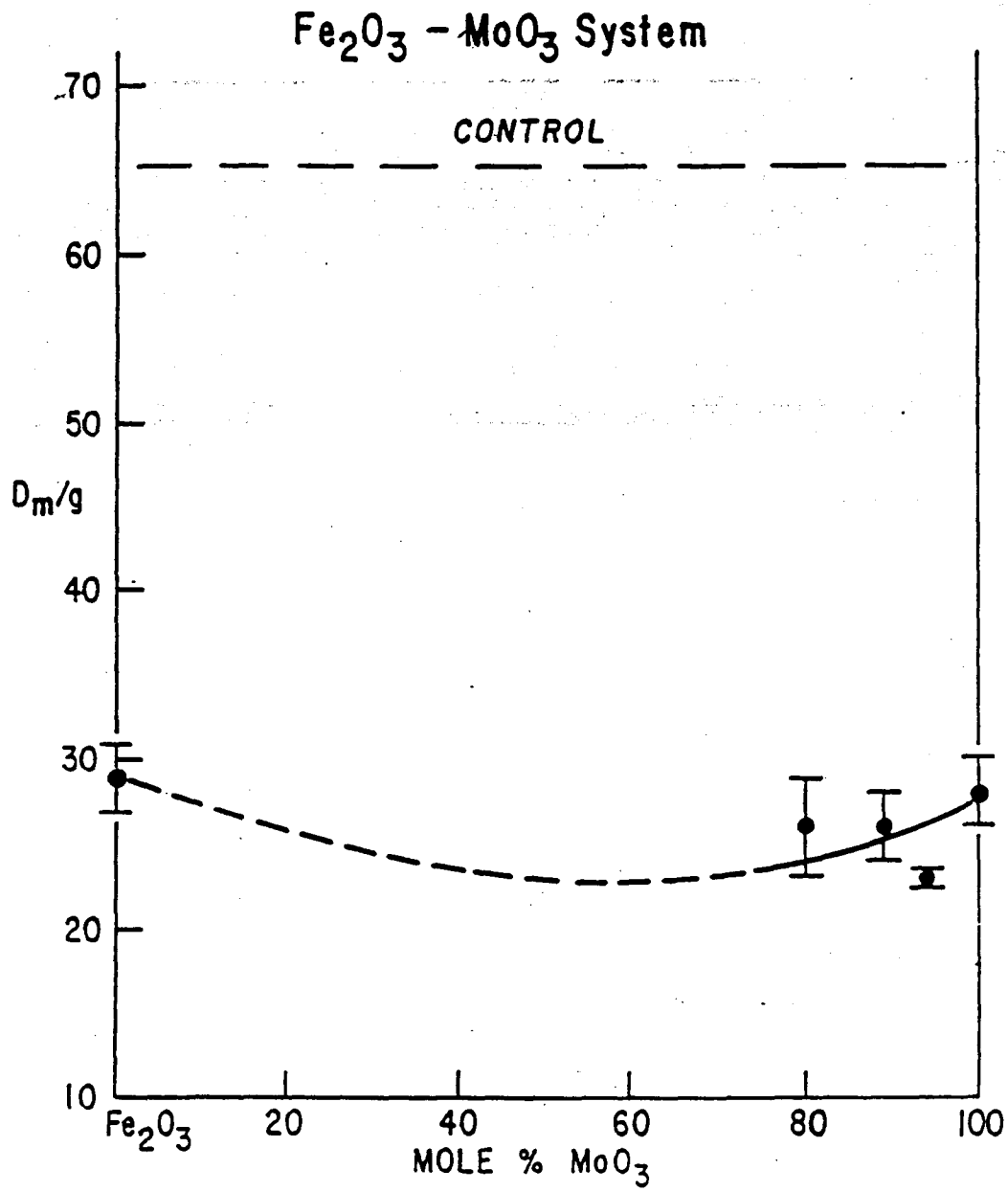

FIGURE 14

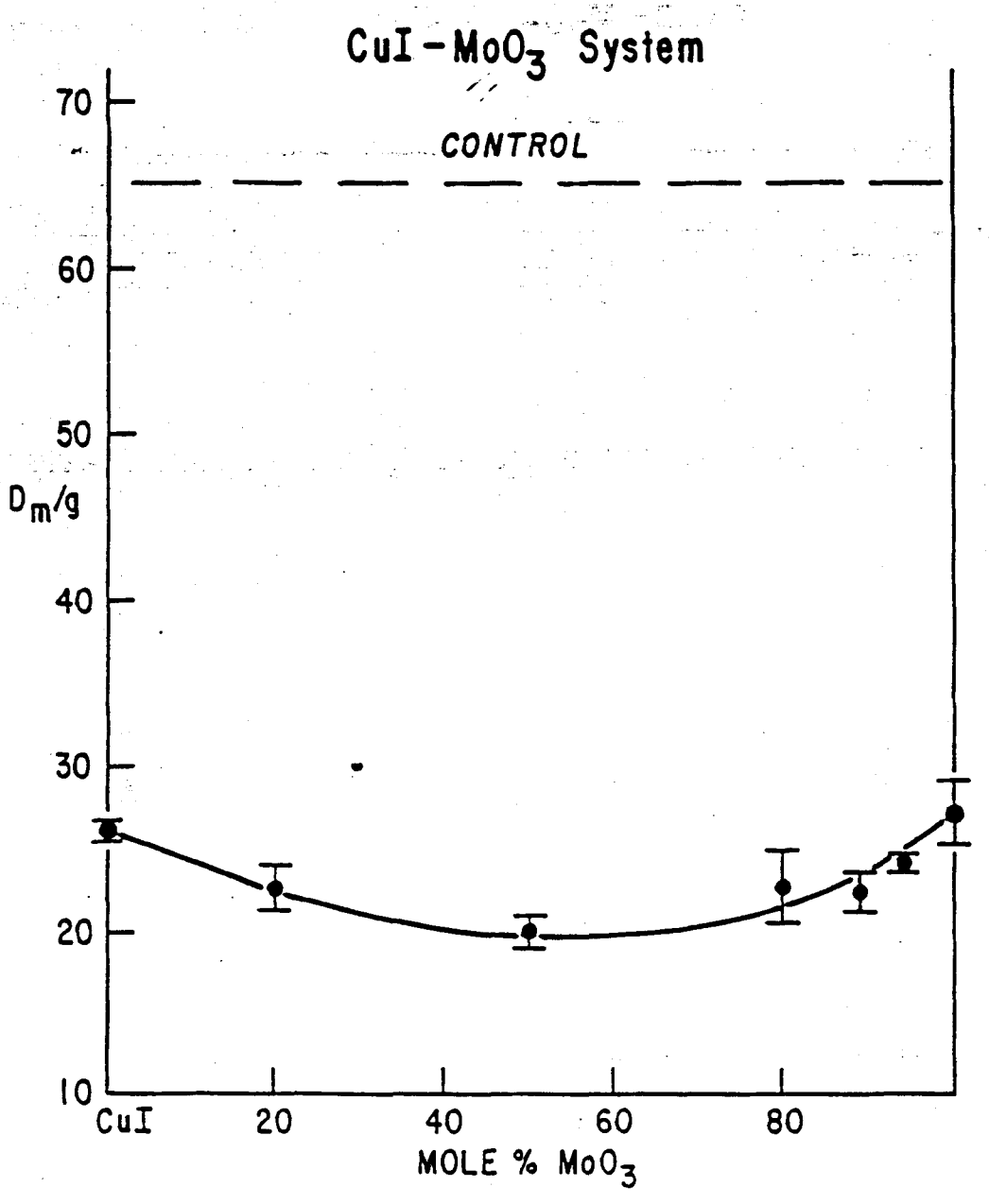

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TABLE 1

Isotopic Distributions of Selected PVC/DPVC Pyrolyzates

Isotopic species $C_lH_mD_n$-MW	Percent abundance		
	Observed[a]	Corrected[b]	Predicted[c]
Benzene			
C_6H_6-78	50	50	50
C_6H_5D-79	2.6	3	0
$C_6H_4D_2$-80	1.5	2	0
$C_6H_3D_3$-81	0.6	<1	0
$C_6H_2D_4$-82	1.4	1	0
C_6HD_5-83	7.5	2	0
C_6D_6-84	36	42	50
Toluene			
C_7H_8-92	23	23	28
C_7H_7D-93	17	17	19
$C_7H_6D_2$-94	8.2	8	3
$C_7H_5D_3$-95	1.7	2	0
$C_7H_4D_4$-96	2.7	3	0
$C_7H_3D_5$-97	4.8	4	0
$C_7H_2D_6$-98	13	10	11
C_7HD_7-99	22	24	28
C_7D_8-100	7.4	9	11
Styrene			
C_8H_8-104	37	37	42
C_8H_7D-105	10	10	8
$C_8H_6D_2$-106	4.1	4	0
$C_8H_5D_3$-107	2.5	2	0
$C_8H_4D_4$-108	0.8	1	0
$C_8H_3D_5$-109	0.7	1	0
$C_8H_2D_6$-110	6.7	4	0
C_8HD_7-111	16	14	17
C_8D_8-112	22	27	33
Indene			
C_9H_8-116	42	42	42
C_9H_7D-117	8.3	8	8
$C_9H_6D_2$-118	4.9	5	0
$C_9H_5D_3$-119	1.9	2	0
$C_9H_4D_4$-120	1.6	2	0
$C_9H_3D_5$-121	4.0	3	0
$C_9H_2D_6$-122	6.0	5	0
C_9HD_7-123	11	7	17
C_9D_8-124	21	26	33
Naphthalene			
$C_{10}H_8$-128	57	57	67
$C_{10}H_7D$-129	5.1	5	0
$C_{10}H_6D_2$-130	0.9	1	0
$C_{10}H_5D_3$-131	0.7	1	0
$C_{10}H_4D_4$-132	0.1	~0	0
$C_{10}H_3D_5$-133	0.8	1	0
$C_{10}H_2D_6$-134	1.0	1	0
$C_{10}HD_7$-135	6.3	1	0
$C_{10}D_8$-136	28	34	33
1- and 2-Methylnaphthalene			
$C_{11}H_{10}$-142	25	25	37
$C_{11}H_9D$-143	18	18	26
$C_{11}H_8D_2$-144	15	15	4
$C_{11}H_7D_3$-145	4	4	0

TABLE 3

Model Rigid PVC Compound: Smoke Formation in the NBS Smoke Chamber Test

Tin stabilizer	D_m/g	σ	n
no	57.6	4.2	6
yes	64.9	9.3	147

TABLE 4

Model Rigid PVC Compound: Smoke and Char Formation in the Smoke–Char Test

Tin stabilizer	S_{PVC}	σ	n	% BC	σ	n
no	103.0	16.9	9	11.0	6.6	9
yes	101.8	14.4	130	8.0	4.2	53

TABLE 6

SMOKE-CHAR CORRELATION - MoO_3

MoO_3 (PHR)	Dm/g	S_{PVC}	% BC
-	55	116	9
2	40	48	28
5	28	43	35
10	21	40	37

TABLE 8

A. Relative Abundances of Selected Pyrolyzates at 550°C

Pyrolyzate	Relative abundance[a]
C_1–C_3 aliphatics	2.3
C_4–C_6 aliphatics	1.5
Methyl and ethyl chlorides	2.9
Benzene	0.20
Toluene	0.91
Dimethyl- and ethylbenzene	0.78
Naphthalene	0.14
Methylnapthalenes	0.35
Biphenyl	0.37
Total aliphatics[b]	2.1
Total aromatics[c]	0.60
Total chloro[d]	~3.

B. Computer Area per mg Sample (Arbitrary Units)

	Total aliphatics[b]	Total aromatics[c]	Total chloro[d]
Control	6,900	25,600	14
MoO_3–PVC	14,200	15,400	42

[a] Ratio of FID-GC peak area of MoO_3–PVC compound to the control compound (average of multiple runs).

[b] Sum of C_1–C_6 aliphatic hydrocarbons.

[c] Sum of all aromatic compounds detected.

[d] Mostly methyl chloride and ethyl chloride.

TABLE 10

Isotopic Distribution of Selected PVC Pyrolyzates[a]

d_x-MW[b]	Control[c]	MoO_3[d]	d_x-MW	Control	MoO_3
	C_2H_4 Ethylene			C_7H_8 Toluene	
d_0-28	12.	3.6	d_0-92	5.1	5.7
d_1-29	16.	22.	d_1-93	14.	8.6
d_2-30	31.	32.	d_2-94	15.	13.
d_3-31	27.	24.	d_3-95	11.	14.
d_4-32	14.	19.	d_4-96	11.	17.
			d_5-97	13.	15.
			d_6-98	16.	13.
			d_7-99	11.	10.
			d_8-100	3.3	4.0
	C_6H_6 Benzene			C_9H_8 Indene	
d_0-78	52.	43.	d_0-116	23.	0.
d_1-79	4.7	10.	d_1-117	11.	3.3
d_2-80	1.3	3.7	d_2-118	9.6	8.5
d_3-81	0.6	3.6	d_3-119	9.2	15.
d_4-82	1.9	4.5	d_4-120	6.9	17.
d_5-83	8.1	9.4	d_5-121	8.3	24.
d_6-84	31.	26.	d_6-122	11.	15.
			d_7-123	11.	12.
			d_8-124	10.	5.3
	$C_{10}H_8$ Naphthalene			$C_{11}H_{10}$ Methylnaphthalene	
d_0-128	45.	23.	d_0-142	10.	2.3
d_1-129	8.7	10.	d_1-143	15.	4.3
d_2-130	4.4	10.	d_2-144	14.	8.7
d_3-131	2.2	7.5	d_3-145	9.6	9.4
d_4-132	1.4	7.1	d_4-146	7.0	17.
d_5-133	1.6	9.9	d_5-147	5.4	18.
d_6-134	3.5	8.7	d_6-148	6.7	15.
d_7-135	11.	9.5	d_7-149	8.9	11.
d_8-136	22.	14.	d_8-150	11.	11.
			d_9-151	8.3	2.5
			d_{10}-152	3.0	1.7

[a] Determined from PY-GC-FI-MS molecular ion intensities; average of duplicate runs. Isotopic abundances have been corrected for the natural abundance of ^{13}C.

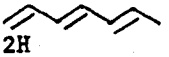
[b] Isotopic species (d_x) and molecular weight (MW).

[c] Percent isotopic abundances for the "control" sample are repeated from ref. 11.

[d] Control plus 10 phr MoO_3.

TABLE 15

Higher-Boiling Products from the Pyrolysis of 2,4,6-Trichloroheptane in the Presence of a Molybdenum Catalyst as Determined by $(GC)^2$-MS

Molecular Weight	Compound	Description
92	$CH_3\phi$	Toluene
106	$C_2\phi$	3 isomers
120	$C_3\phi$	4 isomers - mostly methyl-ethyl
134	$C_4\phi$	4 isomers - many are dimethyl-ethyl and/or methyl-isopropyl
148	$C_5\phi$	7 isomers - some are methyl-diethyl and/or methyl-isobutyl
162	$C_6\phi$	2 isomers
170	C_3Np	Substituted naphthalenes-5 isomers mostly methyl-ethyl and/or isopropyl
184	C_4Np	6 isomers - mostly methyl-isopropyl and/or dimethyl-ethyl and/or diethyl
188	Dimer	2 x  (I)
190	Dimer	I + 2H
198	C_5Np	7 isomers