

The Formation of Volatile Pyrolyzates from Poly(vinyl Chloride)

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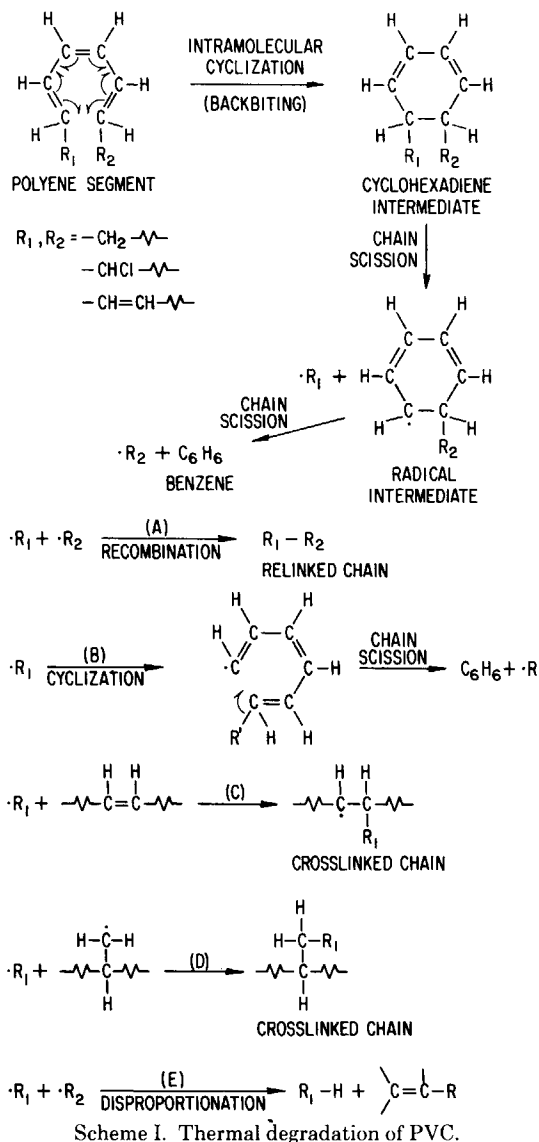
Synopsis

The formation of volatile pyrolyzates in poly(vinyl chloride) has been studied by pyrolysis-gas chromatography-mass spectroscopy. Isotopic distributions of pyrolyzates from experiments with perdeutero-PVC show that pure conjugated aromatic pyrolyzates (e.g., benzene, styrene, naphthalene, biphenyl, anthracene) are formed mostly via intramolecular cyclization. Mixed aromatic-aliphatic pyrolyzates (e.g., toluene, indene, methylnaphthalene) are formed at least partially via intermolecular (crosslinking and/or hydrogen transfer) mechanisms. Direct scission of the PVC chain to form chlorine-containing pyrolyzates is a very minor degradation pathway. Most chlorine-containing "pyrolyzates" from PVC are due to secondary reactions of HCl with the environment or with non-PVC compounding ingredients. No evidence was found for oxygen-containing pyrolyzates derived from the PVC backbone under conditions of nonflaming pyrolysis in air.

INTRODUCTION

The first step in inert atmosphere PVC thermal decomposition is dehydrochlorination. Loss of HCl leaves as a residue a conjugated polyene structure that can undergo further pyrolysis to yield a vast array of hydrocarbon products.¹⁻⁶ The most abundant volatile pyrolyzate from PVC (other than HCl) is benzene. Benzene formation is a facile process and occurs nearly concurrently with the evolution of HCl.⁵ Deuterium labeling experiments using pyrolysis-gas chromatography-mass spectroscopy (PY-GC-MS) have shown that benzene formation is the result of intramolecular cyclization of the polyene chain rather than by crosslinking between neighboring PVC/polyene chains.⁷

Benzene formation evidently occurs via a cyclohexadiene intermediate (Scheme I). Cleavage of the cyclohexadiene to yield benzene plus radical chain ends ($\cdot R_1$ and $\cdot R_2$) is likely a two-step process. Scheme I suggests several possible fates for the radical chain ends. Two radicals from either the same or different polymer chains could recombine to form a new (or relinked) polymer chain (A). If the radical contains a polyene segment, it could cyclize and release additional benzene pyrolyzate (B), forming a new radical chain end ($\cdot R$). The radicals could react with neighboring chains to form crosslinks (C and D). In reaction D, a side-chain radical is involved. This could be formed from a pendent chloromethyl group, a known structural defect in PVC.^{8,9} It should be noted, however, that homolysis of a primary C-Cl bond would not be a favorable process unless allylic. Even then it is uncertain whether this would be a significant source of radicals. Reaction C, on the other hand, seems more favorable as a crosslinking pathway. Crosslinked species might be intermediates leading to formation of volatile pyrolyzates other than benzene. Finally, transfer of a hydrogen atom from one radical to another (disproportionation) is another possible termination step (E).



A recent series of experiments designed to investigate the early stages of PVC thermal degradation has revealed considerable detail about the process.¹⁰⁻¹⁵ In inert atmosphere pyrolysis, GPC data show an increase in polymer molecular weight even in the earliest stages of dehydrochlorination. This indicates that crosslinking of polymer chains takes place very early. Direct chain scission to form aliphatic and chlorine-containing pyrolyzates apparently does not occur to any appreciable extent in the early stages of degradation. Ultraviolet spectroscopy has determined an average polyene sequence length of about 10 double bonds. The formation of more extensive polyene chain segments is prevented by competing degradation pathways (e.g., cyclization and crosslinking). Dehydrochlorination (and hence polyene segment formation) is believed to be initiated primarily at unsaturated sites (allylic chlorines) or at other "defect" sites in the polymer chain.

Several early crosslinking mechanisms in PVC evidently exist. Intermolecular HCl elimination has been suggested as one possibility.¹⁶ Evidence has been presented that HCl may promote crosslinking through a Diels–Alder mechanism,¹⁷ although recent work suggests that the action of HCl is simply to catalyze the dehydrochlorination process.¹⁸ Thus, while there is certainly good experimental evidence for crosslinking in the early stages of PVC degradation, the exact nature of the various crosslinking mechanisms is not well known.

One objective of our current study was to determine if crosslinking mechanisms are important in the formation of volatile pyrolyzates during PVC thermal degradation. Although intermolecular reactions are unimportant in the formation of benzene,⁷ it was not known whether crosslinked species were involved in the formation of other volatile pyrolyzates. The current study was also initiated with respect to smoke retardation in PVC compounds. It was thought that a better understanding of the mechanisms by which volatile pyrolyzates are formed from PVC would provide insight into the mechanisms by which smoke reducing and char forming additives work in PVC compounds. The results presented here describe the use of perdeutero-PVC as a tracer to study volatile pyrolyzate formation from PVC (without additives).

EXPERIMENTAL

A CDS model 100 Pyroprobe (platinum coil probe) was used. Pyrolyses were carried out for 20 sec at 550°C using the fastest temperature rise time available on the pyroprobe. The pyrolyses were conducted in a dry helium or dry air environment at a flow rate of 20–30 cm³/min. The carrier gases were dried with a molecular sieve trap. The pyroprobe was calibrated separately in flowing helium or air environment, using a thermocouple probe for temperature measurement. Pyrolyses were carried out in Pyrex sample tubes open at one end (for helium) or at both ends (for air); plugs of glass wool were used to hold the polymer samples in place. The sample size was ~0.1 mg (for electron impact ionization) or ~2 mg (for field ionization).

The pyrolyzates were analyzed by gas chromatography–mass spectroscopy. The GC–MS system consisted of a Varian 3700 digital gas chromatograph, a Varian MAT 311A mass spectrometer (double focusing), and a Finnigan Inco 2400 data system. System temperatures were as follows: PY–GC interface (injector) 150°C; GC–MS interface (all-glass jet separator) 290°C; ion source 220°C. Two gas-chromatographic columns were used. Lower-boiling pyrolyzates were separated on a 4 m × 2 mm I.D. glass 80/100 mesh Porapak PS column, programmed from 40 to 200°C at 4°/min after an initial 4-min hold. Higher-boiling pyrolyzates were separated on a 4 m × 2 mm I.D. glass 3% Dexsil 300 on 100/120 mesh Supelcoport column, programmed from 50 to 300°C at 5°/min after an initial 4-min hold.

Initial PY–GC–MS runs were made in electron impact (EI) mode (70 eV) using a combination chemical ionization/electron impact (CI/EI) ion source. Pyrolyzate identifications were made by examination of the electron impact fragmentation patterns. Field ionization (FI) was used for PY–GC–MS runs in which isotopic abundances were to be measured. For these experiments a combination field ionization/field desorption/electron impact (FI/FD/EI) ion source was used. Field emitters were prepared with the Varian MAT commercial

apparatus (high-temperature activation). Instrument resolution, $M/\Delta M$, was ~ 1000 (EI mode) or ~ 500 (FI mode) using the 10% valley definition. Data were acquired and processed by computer after calibration of the mass spectrometer with perfluorokerosene in the electron impact mode.

Two PVC samples were used. The "normal" PVC sample was Geon 103EP F76, prepared by suspension polymerization at 50°C . Molecular weight parameters (by GPC) were $\bar{M}_n = 6.2 \times 10^4$ and $\bar{M}_w = 1.2 \times 10^5$. The perdeutero-PVC sample (DPVC) was prepared by the suspension polymerization of $\text{C}_2\text{D}_3\text{Cl}$ (reported deuterium enrichment 97.3%) at 50°C . (The perdeutero-PVC sample was kindly supplied by A. R. Berens and V. L. Folt, The BF Goodrich Company, Brecksville, Ohio.) GPC-derived parameters were $\bar{M}_n = 1.9 \times 10^5$ and $\bar{M}_w = 3.9 \times 10^5$.

RESULTS AND DISCUSSION

Pyrolysis of PVC and Perdeutero-PVC

The PVC pyrograms (PY-GC-MS) and pyrolyzate identifications obtained in this study are very similar to those reported previously.¹⁻⁶ Briefly, the volatile PVC pyrolyzates formed at 550°C in inert atmosphere consist of hydrogen chloride and a wide variety of aromatic and mostly unsaturated aliphatic hydrocarbons; HCl and benzene are the most abundant pyrolyzates.

The PVC and DPVC gave essentially the same distribution of pyrolyzates. Thermogravimetric analysis showed that DPVC is somewhat more stable toward thermal degradation than is normal PVC, but at 550°C this difference in stability was not apparent. Field ionization mass spectra (FIMS) of the molecular ion regions of benzene and toluene are shown in Figure 1. The use of field ionization greatly simplified the spectral interpretation, since essentially the only ions observed were molecular ions.

The volatile pyrolyzates from pure DPVC were predominately, but not totally,

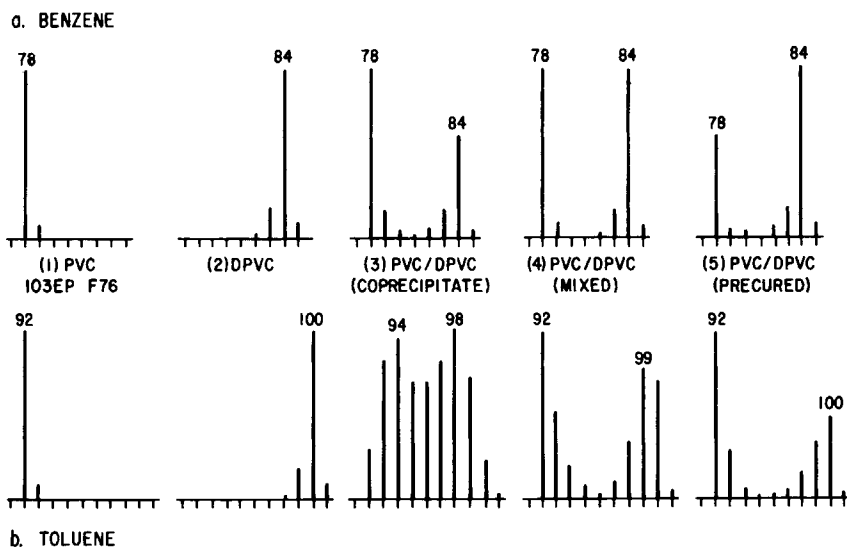


Fig. 1. Field ionization mass spectra of PVC pyrolyzates.

perdeuterated. The deuterium enrichment was measured (using FIMS data) for over 20 pyrolyzates from DPVC, and an average value of $97.6 \pm 0.5\%$ was obtained. It should be noted that the aliphatic pyrolyzates had a slightly higher average deuterium enrichment ($98.1 \pm 0.5\%$) than the aromatic pyrolyzates ($97.3 \pm 0.3\%$). This effect is apparently real, although we can offer no explanation for it. At any length, the average value of 97.6% is within experimental error of the reported monomer—and therefore polymer—enrichment (97.3%). One might expect the deuterium enrichment of the pyrolyzates to be *less* than that of the polymer due to secondary hydrogen/deuterium exchange in the pyrolysis zone, but this clearly has not occurred. Hydrogen/deuterium exchange with the “environment” would tend to complicate the interpretation of the mass spectral data, so it is fortunate that no H/D exchange with the pyrolysis environment was observed.

Formation of Chlorine-Containing Pyrolyzates

PVC in general yields only traces of volatile chlorine-containing hydrocarbons upon pyrolysis.¹⁻⁶ The principal chlorine-containing hydrocarbons detected in the present experiments were methyl chloride, vinyl chloride, ethyl chloride, and chlorobenzene, all at trace levels. It was somewhat surprising to find that methyl chloride “produced” via pyrolysis of DPVC contained mostly ($\sim 95\%$) *n*ondeuterated methyl chloride (CH_3Cl), while the vinyl chloride and chlorobenzene that were produced were essentially fully deuterated ($\sim 95\%$ $\text{C}_2\text{D}_3\text{Cl}$ and $\sim 85\%$ $\text{C}_6\text{D}_5\text{Cl}$). These results show that, while vinyl chloride and chlorobenzene are formed via normal PVC pyrolysis mechanisms, most of the methyl chloride (and ethyl chloride as well) is produced via external reactions. Most likely DCl/HCl produced via pyrolysis reacts with chemical species in the environment to produce the methyl chloride in secondary reactions. This “environment” might be impurities in the PVC or, more likely, materials on the walls of the pyrolysis system.

In general, these perdeutero-PVC results establish conclusively that direct scission of the PVC chain to form chlorine-containing pyrolyzates is a very minor decomposition pathway. The quantities formed seem to be in the parts-per-million range. When enhanced formation of chlorine-containing pyrolyzates is observed in a PVC compound, it is reasonable to assume that HCl (or perhaps Cl_2) has reacted in some way with one or more of the non-PVC recipe ingredients to give the enhanced yield of chlorine-containing pyrolyzates.

One further point can be brought out in this regard. It was recently shown that vinyl chloride is a minor pyrolysis product from PVC; typical levels detected were 15–30 ppm.¹⁹ These amounts are consistent with our experiments.

Effect of Oxygen on Pyrolyzate Formation

Pyrolysis experiments conducted in air were found to produce about the same mix of pyrolyzates as the experiments conducted in an inert atmosphere (helium). A comparison of volatile chlorine-containing aromatics produced by pyrolysis in air versus inert atmosphere does provide an interesting subtlety, however. A slight, but real, increase in chlorine-containing aromatics was noted by PY-GC-EI-MS in the air environment. The only chloroaromatic detected in the

inert atmosphere pyrolyses was chlorobenzene. Several additional chlorine-containing compounds were detected at trace levels (parts per million) in air pyrolyses. These included chlorotoluene, dichlorobenzene (two isomers), trichlorobenzene (two isomers), tetrachlorobenzene (two isomers), and even pentachlorobenzene. This indicates that oxygen, to a very small extent, has promoted the abstraction of hydrogen from PVC chains or else the rechlorination of polyene chains. This same effect has been noted previously.⁶

Another interesting aspect of air pyrolysis is the formation of oxygen-containing hydrocarbons. Only small amounts of oxygen-containing aliphatic hydrocarbons were detected by PY-GC-EI-MS: methanol, ethanol, acetaldehyde, and acetone. No oxygen-containing aromatics were detected, although traces of benzaldehyde and substituted phenols have been reported by Michal.⁶ A most curious fact is that in the air pyrolysis of perdeutero-PVC *all* of the oxygen-containing aliphatics detected were totally *nondeuterated*. Thus, the small amounts of oxygen compounds observed were coming from the environment (probably from oxidation of materials on the walls of the pyrolysis system) and not from oxidation of PVC. These results seem consistent with earlier studies of PVC pyrolysis in oxygen-containing atmospheres; Wooley⁴ and Boettner et al.³ reported no oxygen-containing hydrocarbons in PVC volatile pyrolyzates. Thus, it must be concluded that volatile pyrolyzate formation in PVC is essentially nonoxidative. Under flaming conditions organic pyrolyzates are certainly converted to oxidized products (mostly CO, CO₂, and H₂O), but under non-flaming conditions there is little evidence for the formation of oxygen-containing hydrocarbons from PVC.

Mechanisms of Volatile Pyrolyzate Formation

PY-GC-MS experiments with perdeutero-PVC have proven to be quite valuable in helping to elucidate the mechanisms by which volatile pyrolyzates form in PVC. Table I lists field ionization mass spectra of several pyrolyzates from five different PY-GC-MS experiments at 550°C in helium: (1) PVC (Geon 103EP F76), (2) perdeutero-PVC (DPVC), (3) 50:50 PVC/DPVC (coprecipitate), (4) 50:50 PVC/DPVC (mixed particles), and (5) 50:50 PVC/DPVC (precurd chars). These experiments were chosen to help distinguish among the various mechanistic possibilities, as will be discussed shortly.

The sample for experiment 3 was prepared as follows. Equal weights of PVC and DPVC (~15 mg each) were dissolved in 1.5 cm³ tetrahydrofuran. The polymers were then coprecipitated with 15 cm³ methanol. The solids were collected by filtration and dried under a stream of nitrogen at room temperature. For experiment 4, an equal weight mixture of PVC and DPVC particles (*not* coprecipitated) was pyrolyzed. For experiment 5, quantities of PVC and DPVC were dehydrochlorinated *separately* under helium at 275°C for 60 min. This removed essentially all of the HCl pyrolyzate (and most of the benzene pyrolyzate) from the polymer. Equal weights of the two dehydrochlorinated (or "precurd") chars were ground together in an agate mortar, and the mixture was then pyrolyzed at 550°C in the normal manner.

The isotopic distributions from these five experiments are listed in Table I for several pyrolyzates. The pyrolyzates selected were those whose molecular ion regions were clear of interferences from compounds co-eluting from the gas

TABLE I
 Isotopic Distribution of Selected PVC Pyrolyzates^a

Isotopic species C ₁ H _m D _n —MW	Percent isotopic abundance ^b				
	PVC 103EP F76	DPVC	PVC + DPVC (coprecipitate)	PVC + DPVC (mixed)	PVC + DPVC (precured)
Ethylene					
C ₂ H ₄ —28	100.	—	12.	32.	40.
C ₂ H ₃ D—29	—	—	16.	8.1	9.2
C ₂ H ₂ D ₂ —30	—	1.2	31.	4.3	5.6
C ₂ HD ₃ —31	—	3.7	27.	15.	4.8
C ₂ D ₄ —32	—	95.	14.	41.	41.
Benzene					
C ₆ H ₆ —78	100.	—	52.	46.	33.
C ₆ H ₅ D—79	—	—	4.7	0.0	0.2
C ₆ H ₄ D ₂ —80	—	—	1.3	0.2	0.9
C ₆ H ₃ D ₃ —81	—	—	0.6	0.0	0.3
C ₆ H ₂ D ₄ —82	—	0.8	1.9	0.5	3.1
C ₆ HD ₅ —83	—	15.	8.1	7.4	8.4
C ₆ D ₆ —84	—	84.	31.	46.	54.
Toluene					
C ₇ H ₈ —92	100.	—	5.1	29.	44.
C ₇ H ₇ D—93	—	—	14.	12.	9.1
C ₇ H ₆ D ₂ —94	—	—	15.	4.5	1.8
C ₇ H ₅ D ₃ —95	—	—	11.	1.6	0.6
C ₇ H ₄ D ₄ —96	—	—	11.	0.8	1.0
C ₇ H ₃ D ₅ —97	—	—	13.	2.8	2.2
C ₇ H ₂ D ₆ —98	—	1.1	16.	9.8	6.8
C ₇ HD ₇ —99	—	16.	11.	21.	14.
C ₇ D ₈ —100	—	83.	3.3	19.	20.
Indene					
C ₉ H ₈ —116	100.	—	23.	29.	30.
C ₉ H ₇ D—117	—	—	11.	8.2	11.
C ₉ H ₆ D ₂ —118	—	—	9.6	6.5	11.
C ₉ H ₅ D ₃ —119	—	—	9.2	3.8	3.9
C ₉ H ₄ D ₄ —120	—	—	6.9	2.7	2.9
C ₉ H ₃ D ₅ —121	—	—	8.3	3.1	2.0
C ₉ H ₂ D ₆ —122	—	2.0	11.	7.2	8.0
C ₉ HD ₇ —123	—	17.	11.	15.	11.
C ₉ D ₈ —124	—	81.	10.	24.	20.
Napthalene					
C ₁₀ H ₈ —128	100.	—	45.	44.	44.
C ₁₀ H ₇ D—129	—	—	8.7	2.7	5.4
C ₁₀ H ₆ D ₂ —130	—	—	4.4	1.1	1.8
C ₁₀ H ₅ D ₃ —131	—	—	2.2	0.2	0.7
C ₁₀ H ₄ D ₄ —132	—	—	1.4	0.2	0.4
C ₁₀ H ₃ D ₅ —133	—	—	1.6	0.3	0.9
C ₁₀ H ₂ D ₆ —134	—	0.9	3.5	1.6	3.1
C ₁₀ HD ₇ —135	—	15.	11.	10.	12.
C ₁₀ D ₈ —136	—	84.	22.	39.	32.
1-Methylnapthalene					
C ₁₁ H ₁₀ —142	100.	—	10.	24.	38.
C ₁₁ H ₉ D—143	—	—	15.	16.	12.
C ₁₁ H ₈ D ₂ —144	—	—	14.	8.7	6.7
C ₁₁ H ₇ D ₃ —145	—	—	9.6	4.0	2.2
C ₁₁ H ₆ D ₄ —146	—	—	7.0	1.5	1.3
C ₁₁ H ₅ D ₅ —147	—	—	5.4	0.9	1.0
C ₁₁ H ₄ D ₆ —148	—	—	6.7	1.4	1.3

TABLE I (Continued from previous page)

Isotopic species $C_1H_mD_n$ —MW	Percent isotopic abundance ^b				
	PVC 103EP F76	DPVC	PVC + DPVC (coprecipitate)	PVC + DPVC (mixed)	PVC + DPVC (precurd)
$C_{11}H_3D_7$ —149	—	—	8.9	5.6	5.5
$C_{11}H_2D_8$ —150	—	2.0	11.	9.3	7.1
$C_{11}HD_9$ —151	—	22.	8.3	17.	12.
$C_{11}D_{10}$ —152	—	76.	3.0	11.	12.

^a Determined from PY-GC-FI-MS molecular ion intensities; average of duplicate runs.

^b Isotopic abundances have been corrected for the natural abundance of ^{13}C .

chromatograph. The FI mass spectra were summed over a particular peak eluting from the GC; this generally represented a sum of 8 to 12 spectra (3.0-sec scan cycle time) for each component. (Also note that each perdeutero species eluted a few seconds ahead of its fully hydrogenated counterpart.) The data in Table I have been corrected for the natural abundance of ^{13}C . No corrections for molecular ion fragmentation were necessary, since pure molecular ion spectra were obtained by field ionization. Ionization and detection efficiencies for the various H/D species of a given pyrolyzate were not known, and therefore no corrections could be made in this regard. The data in Table I represent average values from two separate PY-GC-FI-MS runs.

The results from experiment 3 will be considered first (see Table I, column 3). It is apparent that the benzene produced as a pyrolyzate from the PVC/DPVC coprecipitate is mostly C_6H_6 (m/z 78) or C_6D_6 (m/z 84), although there is definitely a few percent abundance of species which show H/D mixing. This is in agreement with O'Mara's earlier work.⁷ Examination of the PVC/DPVC (coprecipitate) mass spectra of naphthalene (Table I) and other "pure" conjugated aromatics not shown (e.g., styrene, biphenyl, anthracene) also shows that these pyrolyzates contain only low abundances of mixed H/D pyrolyzates. Thus, it is clear that these "pure" aromatics are formed mostly via *intramolecular* cyclization (backbiting) in a manner analogous to benzene (Scheme I). The small amounts of mixed H/D pyrolyzates may represent pyrolyzate formation from crosslinked polymer chains or else scrambling from secondary reactions (to be discussed later).

The results for the "mixed" aromatics (i.e., those aromatics with aliphatic substituents) present a distinct contrast, however. Toluene, for example, has as its most abundant isotopic species (Fig. 1 and Table I) $C_7H_6D_2$ and $C_7H_2D_4$ (m/z 94 and 98). Indene, 1-methylnaphthalene (Table I), and other mixed aromatics not listed showed H/D mixing of a similar nature. Finally, note the very marked H/D scrambling of ethylene in Table I. Essentially all low molecular weight aliphatic hydrocarbons observed (C_2 to C_6) showed H/D mixing of a nearly random nature in experiment 3.

There are several mechanisms by which H/D mixing could occur during the pyrolysis experiment: (1) H/D exchange in the chromatographic column, GC-MS interface, or mass spectrometer ion source; (2) secondary reactions of pyrolyzates with the "environment" (e.g., walls of pyrolysis system); (3) secondary vapor phase reactions between pyrolyzates; (4) recombination of HCl/DCl with polyene chains; (5) pyrolyzate formation from crosslinked polymer chains; (6) intermolecular H/D transfer to unsaturated sites or disproportionation.

The first possibility was shown not to be a factor by the following experiment. A quantity of PVC was pyrolyzed in the usual manner, and the pyrolyzates were trapped at the head of the chromatographic column (Dexsil 300) with liquid nitrogen. Subsequently, an equal weight of DPVC was pyrolyzed, and the pyrolyzates were also trapped at the head of the column. The liquid nitrogen trap was then removed, and the GC-MS run was carried out on the mixed pyrolyzates in the normal manner. No mixing of hydrogen and deuterium was observed in any of the pyrolyzates (except for the normal small amount of hydrogen originally present in the DPVC).

The second mechanism (secondary reactions with the environment) is also believed to be unimportant. In the pyrolysis of pure DPVC (experiment 2), the pyrolyzates were found to contain essentially the same deuterium enrichment as the original polymer. Secondary reactions with the pyrolysis environment would have resulted in a decreased deuterium enrichment in at least some of the volatile pyrolyzates.

Experiments 4 and 5 were performed in order to test the latter four mechanistic possibilities. In experiment 4 particles of PVC and DPVC were mixed together (but not coprecipitated) and pyrolyzed. Some H/D mixing was observed in the pyrolyzates (Table I), but not nearly as much as was observed in experiment 3 (coprecipitated PVC/DPVC). In experiment 5 "precured" (dehydrochlorinated) chars of PVC and DPVC were mixed together and pyrolyzed. The H/D scrambling was about the same as that observed in experiment 4, but again the mixing was considerably less than that observed for the PVC/DPVC (coprecipitate) pyrolyzates.

Crosslinking and intermolecular hydrogen transfer could not be factors leading to H/D mixing in either of the above experiments, since in neither case were the PVC and DPVC intimately mixed. Recombination of HCl/DCl with polyene segments was also relatively unimportant, or else more H/D mixing would have occurred in experiment 4 than in experiment 5. Therefore, the logical explanation for the limited H/D scrambling observed in the two experiments is secondary vapor phase reactions between pyrolyzates (or pyrolyzate fragments). These types of high-temperature reactions are common in pyrolysis and tend to complicate the use of deuterium as a tracer.

Thus, the results in Table I suggest that three mechanisms may be principally responsible for producing H/D scrambling in the PVC/DPVC pyrolyzates. Secondary vapor phase reactions definitely occur between pyrolyzates, but the H/D mixing produced via this mechanism (experiments 4 and 5) is not sufficient to account for the mixing observed from the pyrolysis of the PVC/DPVC coprecipitate (experiment 3). It is difficult from these experiments to distinguish between the final two mechanisms—pyrolyzate formation from crosslinked chains and intermolecular H/D transfer. It seems very likely that both mechanisms are operative to produce the aliphatic and mixed aromatic pyrolyzates. Crosslinking is known to occur early in PVC pyrolysis,¹¹⁻¹⁴ so it should not be surprising to find volatile pyrolyzates formed from crosslinked polymer chains. Likewise, transfer of hydrogen atoms to unsaturated sites (either intra- or intermolecularly) must also occur to some extent to explain the saturated and nearly saturated hydrocarbons that are formed during pyrolysis (e.g., C₂H₆, C₃H₈, C₄H₁₀). It has been suggested recently that saturated chain segments (up to C₅H₁₀) may preform in the polymer chain during dehydrochlorination.²⁰ These

could then cleave during high-temperature pyrolysis to give the observed saturated and nearly saturated aliphatics.

Crosslinking implies that one or more carbon atoms from one chain become attached to a neighboring chain. This suggests that the use of ^{13}C -enriched PVC as a tracer would be of value in distinguishing between pyrolyzate formation via crosslinking intermediates and via intermolecular hydrogen transfer mechanisms.

CONCLUSIONS

Experiments using perdeutero-PVC as a tracer have shown that pure conjugated aromatic pyrolyzates in PVC are formed primarily via the intramolecular cyclization (backbiting) route. Mixed aliphatic-aromatic volatile pyrolyzates are formed at least partially via scission reactions of crosslinked polymers and/or intermolecular hydrogen transfer reactions. Low molecular weight aliphatic pyrolyzates are also formed via the more complex intermolecular pathways. Direct scission of PVC chains to form chlorine-containing pyrolyzates is a very minor decomposition pathway. Finally, it has been shown that formation of volatile oxygen-containing pyrolyzates from PVC during nonflaming pyrolysis in air is negligible; volatile pyrolyzate formation in PVC is essentially nonoxidative.

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