

Mechanisms of Formation of Volatile Aromatic Pyrolyzates from Poly(vinyl Chloride)

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Synopsis

The formation of volatile aromatic pyrolyzates in poly(vinyl chloride) has been studied by pyrolysis–gas chromatography–mass spectroscopy. Results from isotopic labeling experiments with perdeutero-PVC suggest that the aromatic pyrolyzates can be divided into three general classes with respect to their formation mechanisms: (1) intramolecular—benzene and naphthalene are formed almost exclusively via intramolecular cyclization reactions; (2) mixed intra/intermolecular—styrene and indene can be formed either intramolecularly or via transfer of one hydrogen atom between PVC chains; (3) intermolecular—toluene and methylnaphthalene can be formed via transfer of one or two hydrogen atoms between chains. The isotopic distributions observed in the labeling experiments can be reasonably well explained without involving crosslinking (intermolecular C–C bond formation) reactions.

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.^{1–9} The most abundant volatile product other than HCl is benzene. 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 or intermolecular hydrogen transfer reactions.^{10,11} The key step leading to benzene evolution is believed to be the formation of a cyclohexadiene intermediate from a polyene segment containing three or more conjugated double bonds.^{12,13}

Our primary objective in this study was to determine the basic mechanisms by which volatile aromatic pyrolyzates form from PVC in the absence of additives. The combustion of aromatic pyrolyzates is the principal source of smoke from burning PVC.^{9,14} Effective smoke retarders for PVC are known to interfere with the normal mechanisms by which volatile pyrolyzates form.^{9,15–17} Thus a good understanding of pyrolysis mechanisms in virgin PVC will 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^{11,17} used GC-field ionization mass spectroscopy (FI–MS) to analyze the volatile pyrolyzates. 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).¹⁸ In the previous study, 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. It was concluded that secondary pyrolysis reactions were enhanced by larger quantities of PVC and gave more H/D mixing than would be expected from primary pyrolyzate formation mechanisms.¹¹

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 earlier pyrolysis of mixtures of PVC and perdeutero-PVC (DPVC), all isotopic species of toluene from $C_7H_8D_0$ to $C_7H_0D_8$ were observed.^{11,17} 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 EI—MS at 38 eV. The smaller amount of PVC resulted in considerably less H/D mixing in the pyrolyzates; i.e., secondary reactions were markedly reduced. Using isotopic abundance data from the 38-eV EI experiments, we have been able to formulate more definitely the mechanisms by which the volatile aromatic pyrolyzates form.

EXPERIMENTAL

A CDS Model 100 Pyroprobe (platinum ribbon probe) was used. Pyrolyses were carried out for 20 s at 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^3/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 Incos 2400 data system.¹¹ 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 $4\text{ m} \times 2\text{ mm ID}$ 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.

The Py—GC—MS runs were made in EI mode (~ 38 eV) using a combination chemical ionization/electron impact ion source. For the aromatic compounds of interest, the molecular ion region showed only M^+ (base peak) and $(M-H)^+$ ions. Control experiments were run in which 20 μg of either PVC (Geon 103EP-F76) or DPVC (97.3 atom-% deuterium¹¹) was pyrolyzed as described above. The data for these runs were used to determine correction factors for the abundances of the $(M-H)^+$ or $(M-D)^+$ ions. In another group of control experiments, 20 μg of PVC was applied to one side of the pyroprobe ribbon and 20 μg of DPVC was applied to the other side (so that the PVC and DPVC were not mixed). Pyrolysis of these samples showed essentially no H/D mixing between the PVC and DPVC pyrolyzates.

The data from the key Py—GC—MS experiment are given in Table I. In this experiment an equal weight mixture of PVC and DPVC (40 μg total) was deposited on the ribbon pyroprobe from tetrahydrofuran solution. The air-dried polymer was pyrolyzed, and the aromatic pyrolyzates were analyzed by GC—MS. Isotopic abundances were determined by EIMS (38 eV). The data in Table I have been corrected for the natural abundance of ^{13}C and also for the abundances of the (M—H) $^+$ and (M—D) $^+$ ions.

MECHANISMS OF FORMATION OF AROMATIC PYROLYZATES

Benzene

The formation of benzene seems well established as a predominantly intramolecular process.⁹⁻¹¹ Dehydrochlorination of PVC leaves as a residue a conjugated polyene which can undergo further pyrolysis to yield hydrocarbon products. In Figure 1 a polyene segment (I) undergoes cyclization to form a cyclohexadiene intermediate (II). Chain scission in two steps (pathway A) leads to benzene (III) via an intramolecular process. Alternatively, chain scission of II followed by hydrogen abstraction from an adjacent chain (disproportionation) leads to intermediate IV. (The notation H* in the scheme refers to abstractable hydrogen which could be either H or D in experiments with mixed PVC/DPVC.) Chain scission of IV followed by hydrogen abstraction would lead to benzene (V) containing zero or one H/D atom from another PVC chain. Pathway A clearly dominates for benzene formation; the data in Table I indicate >90% intramolecular reaction. (Most of the C_6HD_5 species originates from hydrogen (^1H) impurity in the DPVC.) Pathway B is a likely route to explain some of the slight H/D mixing that is observed.

The general validity of Figure 1 (pathway A) seems to be on a firm basis, both experimentally and theoretically.⁹ Experiments on the kinetics of benzene formation suggest that the mechanism consists of several steps.¹⁹ The cyclohexadiene intermediate (II) seems reasonable based on consideration of activation energies.¹² The conversion of II to III is likely a two-step process, since a concerted reaction is not allowed by orbital symmetry.⁹ Also, the presence of macroradical intermediates during PVC decomposition has been verified by ESR experiments.²⁰ 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

Two distinctly different intermolecular pathways for toluene formation are depicted in Figure 2. 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 2 that the two key stable intermediates VII and X can

TABLE I
 Isotopic Distributions of Selected PVC/DPVC Pyrolyzates

Isotopic species $C_1H_mD_n$ -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 I (Continued from previous page.)

$C_{11}H_6D_4$ -146	1	1	0
$C_{11}H_5D_5$ -147	1	1	0
$C_{11}H_4D_6$ -148	3	2	0
$C_{11}H_3D_7$ -149	4	3	0
$C_{11}H_2D_8$ -150	12	11	7
$C_{11}HD_9$ -151	14	16	19
$C_{11}D_{10}$ -152	3	4	7

^a Determined from Py—GC—EI—MS (38 eV) molecular ion intensities; average of five runs.

^b Corrected for 1H abundance (2.7%) in DPVC.

^c Predicted from kinetic isotope effects (see text).

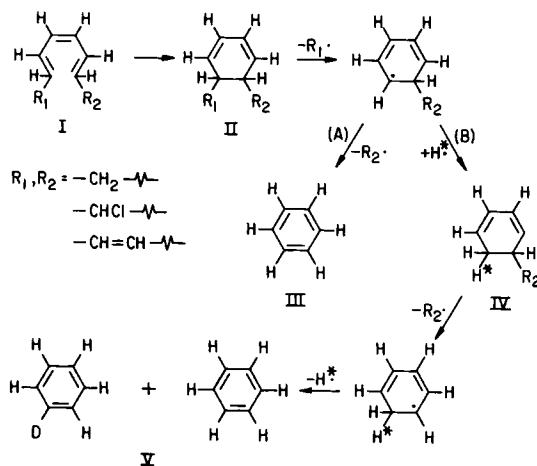


Fig. 1. Benzene formation.

“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.²¹ 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 effect (k_{CH}/k_{CD}) of 2.0, which is reasonable for a high temperature reaction ($\sim 600^\circ C$). The results of the predictions (Fig. 3) show rather good agreement with the actual isotopic abundances (Table I). The most abundant species are C_7H_8 and C_7HD_7 . This agreement suggests that Figure 2 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 2 would be the formation of intermediates in which methyl groups attached to cyclohexadiene rings are “preformed” in the early stages of polymer decomposition. The same cyclohexadiene intermediate (VI) would be the precursor to yield intermediates:



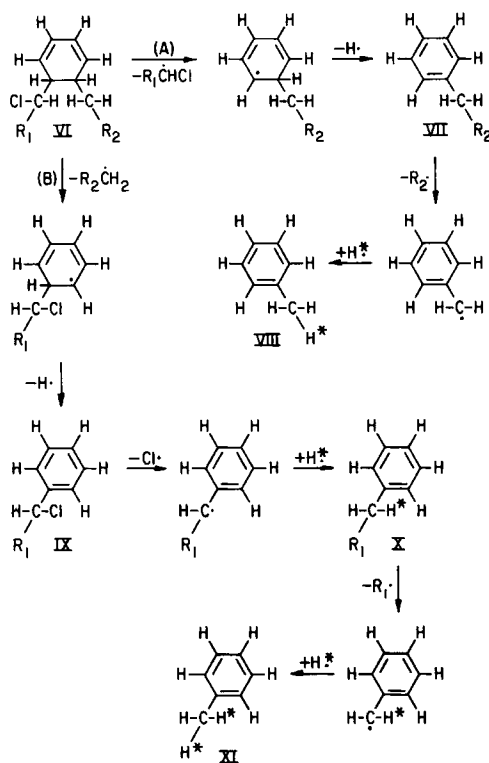


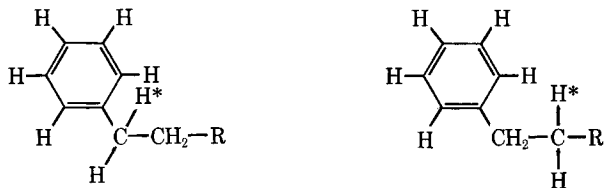
Fig. 2. Toluene formation.

We have no basis for distinguishing between these two variations in Figure 2. In either case the kinetic isotope effect predictions (Fig. 3) would be the same.

Styrene

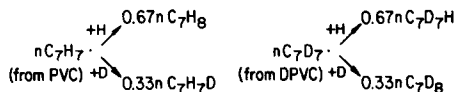
Two different pathways are shown in Figure 4. Pathway A is completely intramolecular, proceeding through intermediate XII to styrene (XIII), showing no intermolecular H/D mixing. Pathway B leads through an intermediate XIV to styrene (XV) in which one intermolecular H/D transfer has occurred. Application of the same analysis used earlier (Fig. 5) gives a predicted isotope distribution in reasonably good agreement with the experiment values (Table I).

One can also envision intermediates of the following types for styrene:

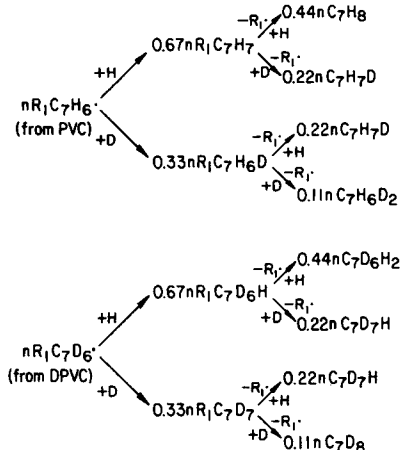


Loss of R^* and H^* would lead to styrene with predicted isotopic abundances: C_8H_8 33, $\text{C}_8\text{H}_7\text{D}$ 17, C_8HD_7 25, and C_8D_8 25. These are in poor agreement with

PATHWAY A, SCHEME II



PATHWAY B, SCHEME II



SUMMATION of the VARIOUS PATHWAYS:

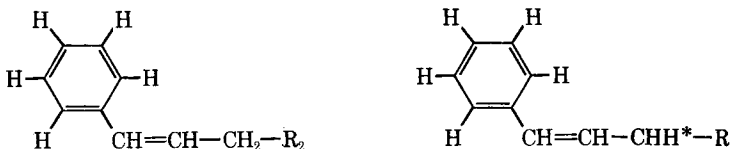
	C ₇ H ₈	C ₇ H ₇ D	C ₇ H ₆ D ₂	C ₇ H ₅ D ₃	C ₇ H ₄ D ₄	C ₇ H ₃ D ₅	C ₇ H ₂ D ₆	C ₇ HD ₇	C ₇ D ₈
TOTAL	1.11n	0.78n	0.11n	0	0	0	0.44n	1.11n	0.44n
PERCENT	28	19	3	0	0	0	11	28	11

Fig. 3. Predicted isotopic abundances for toluene.

the observed values. Though β -substituted styrenes are also potential styrene precursors, they are less attractive intermediates since they first must be converted to relatively unstable vinyl radicals.

Indene

Two pathways for indene formation are shown in Figure 6. Pathway A involves one intermolecular H/D transfer, and pathway B is intramolecular. The predicted isotope distribution is thus the same as for styrene (Fig. 5) and in reasonable agreement with the experimental values (Table I). Intermediates of the following types are also possible:



The isotope distributions predicted for these precursors are the same as those in Figure 6.

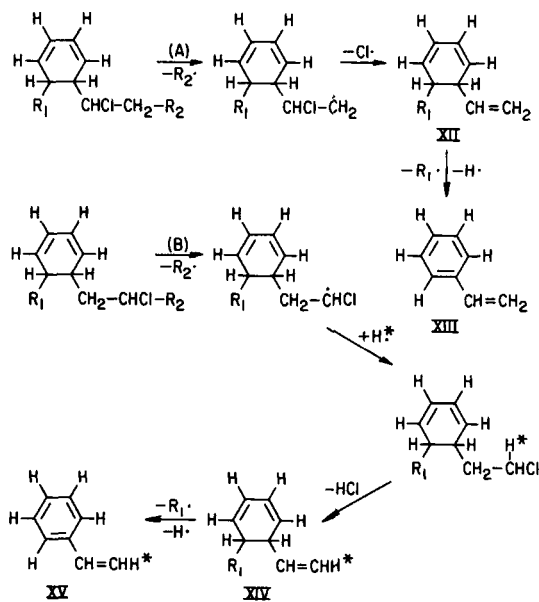


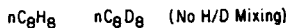
Fig. 4. Styrene formation.

Naphthalene

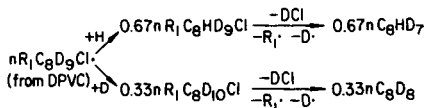
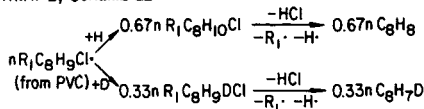
The high abundances of C_{10}H_8 and C_{10}D_8 (Table I) suggest that naphthalene formation is mostly (>90%) intramolecular. Figure 7 suggests a cyclodecatriene intermediate for naphthalene; other closely related variations of Figure 7 also can be drawn.

The higher abundance of C_{10}H_8 compared to C_{10}D_8 (Table I) suggests that there is a kinetic preference for forming the naphthalene ring from PVC as compared to DPVC. If the rate determining step is a proton (deuteron) abstraction from an intermediate, then a primary isotope effect $k_{\text{CH}}/k_{\text{CD}} \cong 2$ would

PATHWAY A, SCHEME III



PATHWAY B, SCHEME III



SUMMATION of the VARIOUS PATHWAYS:

	C_8H_8	$\text{C}_8\text{H}_7\text{D}$	$\text{C}_8\text{H}_6\text{D}_2$	$\text{C}_8\text{H}_5\text{D}_3$	$\text{C}_8\text{H}_4\text{D}_4$	$\text{C}_8\text{H}_3\text{D}_5$	$\text{C}_8\text{H}_2\text{D}_6$	C_8HD_7	C_8D_8
TOTAL	1.67n	0.33n	0	0	0	0	0	0.67n	1.33n
PERCENT	42	8	0	0	0	0	0	17	33

Fig. 5. Predicted isotopic abundances for styrene.

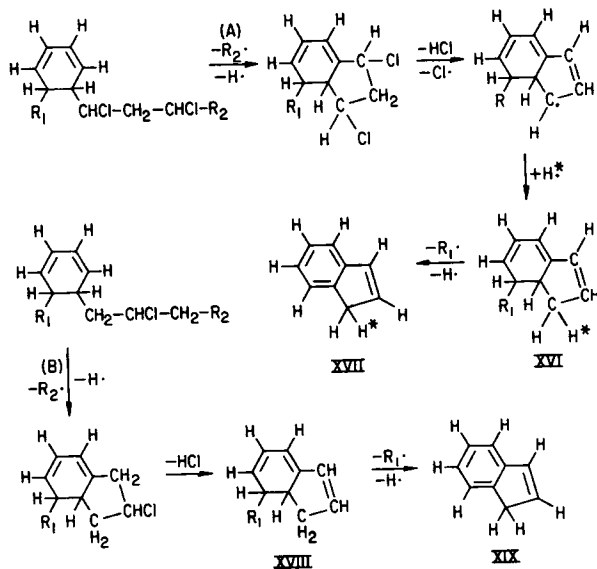


Fig. 6. Indene formation.

be expected. This prediction is in good agreement with the observed isotopic distribution (Table I).

Methylnaphthalene

For methylnaphthalene (Fig. 8) ring formation is analogous to naphthalene (Fig. 7), and methyl group formation is analogous to toluene (Fig. 2). Pathway A (Fig. 8) leads to 2-methylnaphthalene in which one intermolecular H/D transfer has occurred, and pathway B involves two intermolecular H/D transfers. The formation of 1-methylnaphthalene as depicted in abbreviated form (pathway C, Fig. 8) results in the same isotopic distribution as for the 2-methyl isomer. The data in Table I are a combination of the 1-methyl and 2-methyl isomers, which are formed in approximately equal abundance from PVC pyrolysis.

The kinetic isotope effect should be a combination of the effects for naphthalene ring formation and methyl group formation. That is, there should be $\sim 2/1$ preference for ring formation from PVC as compared to DPVC, and the methyl group formation should be governed by the same considerations as for toluene (Fig. 3). The observed and predicted isotopic distributions (Table I) show the general trend expected. However, there does seem to be less agreement in the observed vs. predicted data for methylnaphthalene than for the other aromatic pyrolyzates studied. In particular, the $C_{11}H_8D_2$ species and perhaps

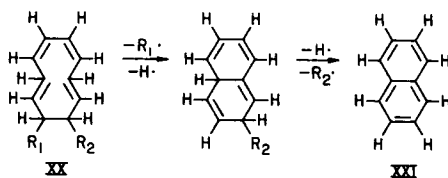


Fig. 7. Naphthalene formation.

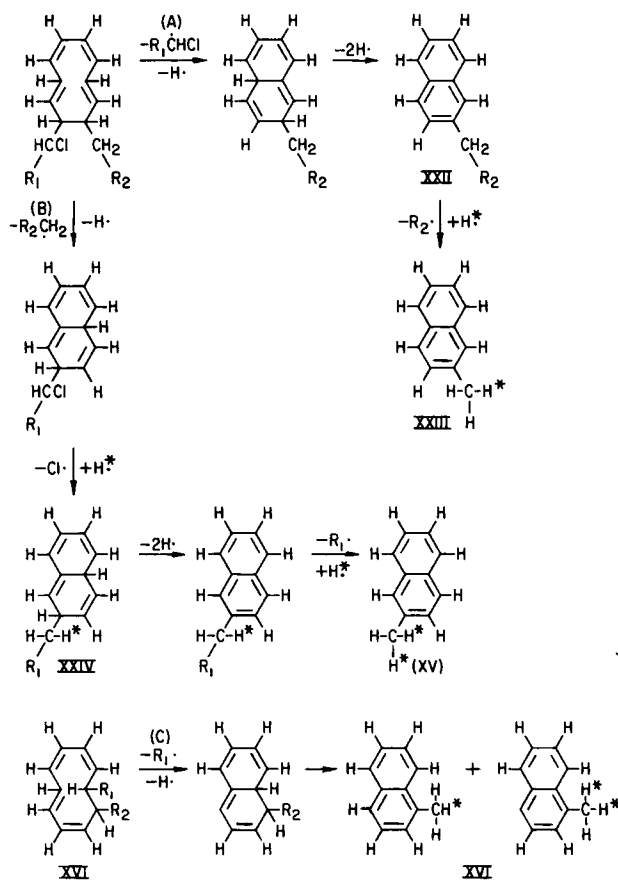


Fig. 8. Methylnaphthalene formation.

also $C_{11}H_2D_8$ are more abundant than would be expected from the isotope effect predictions. We are not sure of the significance of these higher values. Perhaps an additional mechanism that increases the abundance of these species is operative.

DISCUSSION AND CONCLUSIONS

As discussed in the introduction, our earlier Py—GC—FI—MS deuterium studies used relatively large quantities of PVC (~ 2 mg).¹¹ However, the Py—GC—EI—MS technique used in this study permitted the use of much smaller PVC samples (~ 40 μ g). The smaller samples showed less H/D mixing in the pyrolyzates. Using the results from the smaller samples, which more closely reflect the chemistry on the molecular level, we are able to propose mechanisms which explain the formation of all of the important volatile aromatic pyrolyzates. Our results clearly emphasize that the size of the sample and the scale of an experiment must be carefully chosen based on the experimental objectives. This is an important axiom in both analytical chemistry and materials testing.

In the case of our pyrolysis experiments, the main effect is probably related to the kinetics of the pyrolysis reaction and the residence time of the sample and

its initial thermal degradation products in the pyroprobe. The longer residence time for the larger 2-mg samples apparently permitted secondary pyrolysis reactions to occur. These resulted in more H/D mixing in the pyrolyzates than would be expected from the primary pyrolysis reactions. Many of these secondary reactions are intermolecular in nature.¹¹

Aromatic Pyrolyzate Formation

Our results establish conclusively that intermolecular hydrogen transfer (disproportionation) reactions are important in the formation of some volatile aromatic pyrolyzates from PVC. This general conclusion was stated previously,¹¹ but definitive mechanisms were not proposed. The current results suggest that the aromatic pyrolyzates can be divided into three general classes with respect to their formation mechanisms:

1. *Intramolecular*: Benzene and naphthalene are formed almost exclusively via intramolecular cyclization reactions. Biphenyl and anthracene should also fall into this category.

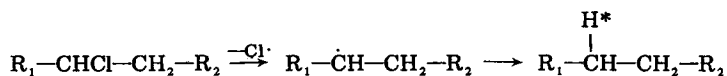
2. *Mixed intra/intermolecular*: Styrene and indene can be formed either intramolecularly or via transfer of one hydrogen atom between chains.

3. *Intermolecular*: Toluene and methylnaphthalene can be formed via transfer of one or two hydrogen atoms between chains. The formation of other alkyl-substituted aromatics would also involve intermolecular reactions (e.g., ethylbenzene, indane, ethylnaphthalene). The formation of longer alkyl groups would involve multiple transfers of hydrogen atoms between chains.

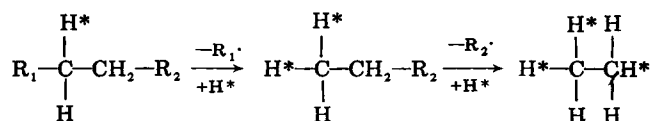
The isotopic distributions of the aromatic pyrolyzates formed from mixed PVC/DPVC can be reasonably well explained without invoking crosslinking (intermolecular C—C bond formation) reactions. Pyrolyzate formation via crosslinked polymer chains would be difficult to detect in these experiments, however, since the carbon atoms were not labeled. Experiments are planned with ¹³C-enriched PVC that should establish conclusively whether or not crosslinking reactions are significant in the formation of volatile aromatic pyrolyzates.

Aliphatic Pyrolyzates

The formation of aliphatic pyrolyzates was not investigated in this work. It has been suggested, however, that saturated chain segments can preform in the polymer during dehydrochlorination, and that scission reactions of these segments lead to volatile aliphatic pyrolyzates.^{11,22} Formation of these segments would involve hydrogen transfer reactions of the type:



Chain scissions leading to volatile aliphatics would involve additional hydrogen transfer:



Very extensive H/D mixing in the aliphatic pyrolyzates from PVC/DPVC experiments was reported earlier.¹¹ Such extensive mixing would be expected from these types of reactions. Further studies to elucidate the mechanisms of aliphatic pyrolyzate formation are planned.

Note added in proof: Recent pyrolysis experiments with mixed PVC/¹³C-PVC are consistent with the mechanistic conclusions stated in this report.

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