Identification of Isomeric Structures of Phenyl and Trimethylsilyl Substituted 1-Alkenes by Gas Chromatography

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Summary

Gas chromatographic retention indices had been measured on two different stationary phases for phenyl and trimethylsilyl substituted 1-alkenes formed during the pyrolysis of a styrene – trimethylvinyl silane copolymer. Retention index differences due to the alteration of trimethylsilyl to phenyl substituent groups at different positions in the molecules of the 1-alkene skeleton were determined. Based on these values the isomeric structure of the pyrolysis products has been identified by determining the position of the trimethylsilyl and phenyl groups in these substituted 1-alkenes. The results correspond to the mechanism of the copolymer’s thermal degradation.

Introduction

Pyrolysis gas chromatographic investigations had been carried out in our laboratory on a copolymer of styrene with trimethylvinyl silane [1]. Monomers and higher molecular weight polymer chain fragments were identified by mass spectrometry as the main degradation products. However, the determination of the isomeric structure of the compounds containing both comonomer units (phenyl and trimethylsilyl substituted 1-alkenes) was not possible based on the mass spectra. Therefore, we have defined these isomeric compounds according to their retention indices.

The retention index of a compound on a given stationary phase is closely connected with the molecular weight, as well as with the composition and shape of the molecule [2, 3].

The difference between the retention indices of a given compound measured on a polar and a non-polar stationary phase (ΔI) is considered to be characteristic of the gas chromatographic “polarity” of the sample molecule; in other words, this value reflects the difference in the interactions of sample and stationary phases of different polarity [4]. Functional groups or some structural features having a functional group character may be characterized by the ΔI values. The difference between the retention indices of two compounds on the same stationary phase (ΔI) may correspond to specific structural differences of the sample pair [2].

Having measured the retention indices of phenyl and trimethylsilyl substituted 1-alkenes of known structure, we have first established the index differences (ΔI) being characteristic for certain substituent group alterations and for the simultaneous changes in intramolecular interactions. Consequently we established the isomeric structure of the analogous compounds of unknown structure by comparing the index differences corresponding to substituent group alterations at known and unknown positions.

Materials

Four groups of isomers formed in the pyrolysis process had been studied.

1. 1,3-substituted 1-propene
   Substituent groups: one trimethylsilyl (T) one phenyl (P)
   Symbol: C3PT
   Number of possible isomers: 2
   Number of isomers studied: 1

2. 2,4-substituted 1-butene
   Substituent groups: one trimethylsilyl (T) one phenyl (P)
   Symbol: C4PT
   Number of possible isomers: 2
   Number of isomers studied: 1

3. 2,4,6-substituted 1-hexene
   Substituent groups: two trimethylsilyl (T) one phenyl (P)
   Symbol: C4PT2
   Number of possible isomers: 3
   Number of isomers studied: 2

4. 2,4,6-substituted 1-hexene
   Substituent groups: one trimethylsilyl (T) two phenyl (P)
   Symbol: C6P2T
   Number of possible isomers: 3
   Number of isomers studied: 2

For the reference compounds of known structure we have used the following symbols:

- C2T: trimethylvinyl silane
- C2P: styrene
- C3T2: 1,3-di(trimethylsilyl) 1-propene
- C4T2: 2,4-di(trimethylsilyl) 1-butene
- C4P2: 2,4-diphenyl 1-butene
- C6T3: 2,4,6-tri(trimethylsilyl) 1-hexene
- C6P3: 2,4,6-triphenyl 1-hexene
Table I. Retention index values measured at four temperatures on OV–101 and OV–225 stationary phases

<table>
<thead>
<tr>
<th>Symbol of compound</th>
<th>Temperature °C</th>
<th>60</th>
<th>120</th>
<th>160</th>
<th>180</th>
<th>160–180</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3T</td>
<td>553</td>
<td>537</td>
<td>16</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C3P</td>
<td>1096</td>
<td>873</td>
<td>223</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C3T2</td>
<td>979</td>
<td>980</td>
<td>-1*</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>C3PT</td>
<td>1403</td>
<td>1235</td>
<td>168</td>
<td>1442</td>
<td>1257</td>
<td>185</td>
</tr>
<tr>
<td>C4T2</td>
<td>1046</td>
<td>1056</td>
<td>-10*</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C4PT</td>
<td>1507</td>
<td>1340</td>
<td>167</td>
<td>1543</td>
<td>1360</td>
<td>183</td>
</tr>
<tr>
<td>C4P2</td>
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<td>–</td>
<td>–</td>
<td>2064</td>
<td>1666</td>
<td>398</td>
</tr>
<tr>
<td>C6T3</td>
<td>1414</td>
<td>–</td>
<td>–</td>
<td>1403</td>
<td>1450</td>
<td>-47*</td>
</tr>
<tr>
<td>(C6PT2)A</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1868</td>
<td>1732</td>
<td>136</td>
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<tr>
<td>(C6PT2)B</td>
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<td>–</td>
<td>–</td>
<td>1934</td>
<td>1774</td>
<td>160</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(C6P2T)B</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>C6P3</td>
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<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* The negative value of ΔI means that OV–225 is less “polar” relative to the corresponding silane compounds than OV–101.

Gas Chromatographic Conditions

The retention index measurements were carried out in a Perkin-Elmer Model 900 gas chromatograph, using 20-m long glass capillary columns coated with OV 101 and OV 225 liquid phases. The number of theoretical plates measured for n-nonane at 60 °C was 30,000 and 27,000 respectively.

Results

The retention index values are given in Table I. The absolute standard deviation in replicate measurements was never above 1 index unit. The ΔI values are also included in the table. They represent the differences of the retention indices measured on the two stationary phases.

On the basis of these ΔI values it is very easy to differentiate a trimethylsilyl substituted compound from one with phenyl substitution, the latter having a much higher ΔI. At the same time this value also differs significantly in isomers.

Among the measured compounds there are several pairs having a similar carbon skeleton but differing in one substituent group. Table II lists the ΔI values for OV-101 and OV-225 stationary phases resulting from the alteration of one trimethylsilyl group to one phenyl group in different molecules. The Δ(ΔI) values, represent the more concise data for the characterization of this group alteration and reflect the changes in “gas chromatographic polarity” caused by the structural differences of the sample pair. These values are also given in the Table II. In the last columns of this table the results of the isomer identification are summarized, by giving the position of the group alteration and the change in intramolecular interaction caused by this alteration.

Let us consider what kind of changes may be expected in the intramolecular interactions of a 1-alkene molecule, if the side-groups were changed from trimethylsilyl to phenyl group.

The general formula of the investigated 1-alkenes can be written as:

\[
\begin{align*}
X & \quad |CH_2| \quad CH_2 \quad CH_2 \quad CH_2 \quad CH_2 \\
2 & \quad 4 & \quad 5 & \quad 6 & \quad 1
\end{align*}
\]

where \(X = P\) or \(T\).

In these molecules the double bond is in conjugation with both phenyl and trimethylsilyl groups substituted at the first or second carbon atom. This conjugation itself may cause a retention increment, since the conjugation with trimethylsilyl — as opposed to conjugation with phenyl — decreases the polarizability of the vinyl group [5]. At the same time for the trimethylsilyl group at the fourth carbon atom, a secondary intramolecular interaction with the double bond is sterically possible. This secondary interaction is expected to lower the ΔI value. The result of this interaction may be different depending on the nature of the substituent group at the second carbon, since due to the primary conjugative effect, the polarizability of the double bond and consequently the ΔI lowering effect of the intramolecular interaction, is higher for a phenyl substituent than for a trimethylsilyl substituent at the second carbon atom.

On this basis of the Δ(ΔI) data given in Table II we can find the proper position of the different substituents in the isomeric molecules, as detailed below.