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## COMPARISON OF DEGRADATION PRODUCTS AND PROCESSES IN MASS SPECTROMETRY AND PYROLYSIS GAS CHROMATOGRAPHY APPLIED TO THE IDENTIFICATION OF ALKYL BENZENES

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### SUMMARY

A comparative study has been made of the pyrolytic and electron-impact degradation processes as used in the identification of alkylbenzenes. The degree of conversion, the yield of the main degradation products and the products produced by different degradation mechanisms show the advantage of pyrolysis gas chromatography over mass spectrometry. The results obtained in the investigation of mono-, di- and poly-substituted alkylbenzenes by both techniques are discussed.

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### INTRODUCTION

Pyrolysis gas chromatography bears some similarities to mass spectrometry in giving reliable data about degraded samples<sup>1</sup>. These similarities are of considerable importance in the identification of alkylbenzenes, as shown in our previous papers<sup>2-4</sup>.

The aim of this work was to make a comparative study of the use of particular pyrolytic and electron-impact degradation products in the differentiation of alkylbenzene homologues and isomers, on the basis of degrees of sample conversion, yields of the main degradation products and the products produced by different degradation mechanisms.

### EXPERIMENTAL

Pyrolysis of alkylbenzenes was performed in a tubular flow micro-reactor with a gold capillary (1119 mm × 1.2 mm I.D.) as described earlier by Cramers and Keulemans<sup>5,6</sup>. A digital voltmeter and a chromel-alumel thermocouple were used for measuring the temperature of pyrolysis. The reactor was connected directly to a gas chromatograph (Becker, Model 1452 DPF) equipped with a flame-ionization detector.

The investigation of the pyrolysis of alkylbenzenes was performed in two steps: (a) the determination of gaseous products (C<sub>1</sub>-C<sub>5</sub>) and (b) the determination of heavier products (C<sub>5</sub>-C<sub>12</sub>). In the first step, the glass column (15 m × 0.8 mm I.D.) containing phenyl isocyanate on Porasil C (180-200 μm), micropacked, was operated

at 70° with a flow-rate of carrier gas (helium) of 2.2 ml/min and a splitting ratio of 1:14. In the second step, the glass column (25.5 m × 0.5 mm I.D.) containing silicone rubber GE SE-30 (open tube) was operated at 65° with a flow-rate of carrier gas (helium) of 1.5 ml/min and a splitting ratio of 1:67. In each instance the reactor temperature was 595°, the reaction time 20 sec and the sample size 0.3 μl. The alkylbenzenes were API standard samples.

For sample injection, a 1-μl Hamilton syringe equipped with a Chaney adaptor for reproducible injections was used.

An Infotronics Model CRS 11 HB digital readout system was used for quantitative interpretation of the pyrograms obtained.

A Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer (10 in. radius, 180°) was used to obtain the mass spectra, with an ionizing voltage of 70 V and ionizing current of 9 mA. The scan was performed by varying the ion-accelerating voltage.

## RESULTS AND DISCUSSION

Benzene and its homologues possess very stable structures and are resistant to thermal degradation and to electron impact. In general, their stability decreases as the molecular weight and the number of substituents on the aromatic ring increase. In spite of the considerable differences between the electron-impact and pyrolysis degradation mechanisms, the pyrolysis conversion and the probability of decomposition in the ion source of a mass spectrometer could be studied by comparison. These differences originate from the energy of decomposition, which is very high when electron impact is applied.

The probability of the decomposition of molecular ions by electron impact is expressed by the equation

$$W_z = \frac{\Sigma I_f}{\Sigma_{25}}$$

where  $\Sigma I_f$  is the sum of all fragment-ion intensities and  $\Sigma_{25}$  is the sum of all ion intensities from the start ( $m/e$  25) to the end of the mass spectrum<sup>7</sup>.

In Table I are presented the results of the pyrolysis conversion of mono-*n*-alkylbenzene and the probability of decomposition of molecular ions in the ion source of the mass spectrometer.

The degree of pyrolysis conversion and electron-impact decomposition related to the size of the *n*-alkyl substituents in mono-*n*-alkylbenzenes is shown in Fig. 1.

It is evident that the degree of conversion in the pyrolysis undergoes distinct changes, depending on the number of carbon atoms in the substituent, while the probability of conversion in electron-impact degradation remains similar for all homologues. The discrepancy in curve A for *n*-butylbenzene could be explained by the mechanism of pyrolysis of *n*-butylbenzene, which differs from that of, *e.g.*, *n*-propylbenzene owing to the more facile cleavage of the weaker C-C bond in the  $\gamma$ -position<sup>4,9</sup>.

The relationship between pyrolysis conversion and the probability of electron-impact decomposition, depending on the position of the substituent in dialkyl-

TABLE I

CONVERSION OF ALKYL BENZENES BY PYROLYSIS AND ELECTRON IMPACT

PGC = Pyrolysis gas chromatography; MS = mass spectrometry.

| Compound*                      | PGC conversion (%) | MS probability of mol. ions conversion, $W_z$ (%) | PGC main product (%) | MS base peak relative to $\Sigma_{25}$ (%) |
|--------------------------------|--------------------|---|----------------------|--|
| Benzene                        | —                  | —   | —                    | 40.40                                      |
| Toluene                        | 0.6                | 77.2  | 83.3                 | 32.55                                      |
| Ethylbenzene                   | 20.7               | 88.2  | 62.3                 | 40.23                                      |
| <i>p</i> -Xylene               | 0.8                | 83.2  | 87.5                 | 28.22                                      |
| <i>m</i> -Xylene               | 0.7                | 83.6  | 73.0                 | 30.15                                      |
| <i>o</i> -Xylene               | 1.3                | 84.5  | 76.9                 | 30.59                                      |
| <i>i</i> -PrB                  | 41.7               | 91.0  | 43.3                 | 38.88                                      |
| <i>n</i> -PrB                  | 49.1               | 91.2  | 53.7                 | 45.17                                      |
| 1-Me-3-EtB                     | 10.9               | 89.7  | 68.9                 | 36.83                                      |
| 1-Me-4-EtB                     | 11.4               | 89.8  | 70.2                 | 39.04                                      |
| 1-Me-2-EtB                     | 21.1               | 89.9  | 51.7                 | 37.09                                      |
| 1,3,5-tri-MeB                  | 0.7                | 83.5  | 86.6                 | 30.20                                      |
| <i>tert.</i> -BuB              | 79.5               | 94.4  | 34.7                 | 25.35                                      |
| 1,2,4-tri-MeB                  | 0.9                | 85.7  | 51.3                 | 31.54                                      |
| <i>i</i> -BuB                  | 71.5               | 91.9**  | 24.8                 | 34.60**                                    |
| <i>sec.</i> -BuB               | 74.3               | 93.3  | 25.7                 | 40.46                                      |
| 1-Me-3- <i>i</i> PrB           | 36.2               | 90.5**  | 45.8                 | 35.70**                                    |
| 1-Me-4- <i>i</i> PrB           | 38.0               | 92.0  | 44.5                 | 35.80                                      |
| 1,2,3-tri-MeB                  | 1.7                | 86.3  | 60.0                 | 31.06                                      |
| 1-Me-2- <i>i</i> PrB           | 47.9               | 91.5  | 28.8                 | 35.81                                      |
| 1,3-di-EtB                     | 19.7               | 91.6  | 65.5                 | 20.90                                      |
| 1-Me-3- <i>n</i> -PrB          | 42.1               | 91.4  | 52.7                 | 39.63                                      |
| <i>n</i> -BuB                  | 49.6               | 92.3  | 39.7                 | 33.61                                      |
| 1,4-di-EtB                     | 23.3               | 91.8  | 66.1                 | 22.35                                      |
| 1,2-di-EtB                     | 27.8               | 91.8  | 48.2                 | 18.51                                      |
| 1-Me-4- <i>n</i> -PrB          | 46.3               | 92.1  | 48.6                 | 45.18                                      |
| 1-Me-2- <i>n</i> -PrB          | 54.9               | 91.7  | 33.5                 | 43.31                                      |
| 1,3-di-Me-5-EtB                | 11.3               | 89.1  | 67.0                 | 32.85                                      |
| 1,4-di-Me-2-EtB                | 21.6               | 89.8  | 49.0                 | 31.43                                      |
| 1-Me-3- <i>tert.</i> -BuB      | 50.7               | 92.9**  | 39.0                 | 28.84**                                    |
| 1,3-di-Me-4-EtB                | 26.4               | 90.8  | 45.1                 | 36.66                                      |
| <i>tert.</i> -PeB              | 95.6               | —   | 41.3                 | —  |
| 1,2-di-Me-4-EtB                | 14.3               | 90.0  | 63.7                 | 34.82                                      |
| 1,3-di-Me-2-EtB                | 38.5               | 90.6  | 32.1                 | 35.36                                      |
| 1-Me-4- <i>tert.</i> -BuB      | 61.3               | 93.0**  | 46.5                 | 30.70**                                    |
| <i>sec.</i> -PeB               | 74.4               | —   | 32.1                 | —  |
| 1,2-di-Me-3-EtB                | 27.8               | 90.2  | 45.0                 | 33.34                                      |
| 1,2,4,5-tetra-MeB              | —                  | 85.2**  | —                    | 27.45**                                    |
| 1,2,3,5-tetra-MeB              | 1.8                | 83.6**  | 60.0                 | 31.07**                                    |
| 1,3-di- <i>i</i> -PrB          | 58.4               | 91.6**  | 36.3                 | 23.18**                                    |
| <i>n</i> -PeB                  | 56.7               | 93.3  | 37.9                 | 28.18                                      |
| 1,2,3,4-tetra-MeB              | 2.2                | —   | 50.0                 | —  |
| 1,4-di- <i>i</i> -PrB          | 64.0               | 93.5  | 33.0                 | 26.78                                      |
| 1,3-di-Me-5- <i>tert.</i> -BuB | 34.2               | 93.5**  | 19.9                 | 25.72**                                    |
| <i>n</i> -HexB                 | —                  | 94.5  | —                    | 24.71                                      |
| <i>n</i> -HeptB                | —                  | 95.4**  | —                    | 26.67                                      |
| <i>n</i> -OctB                 | —                  | 94.4  | —                    | 24.93                                      |

\* B = benzene; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; Hex = hexyl; Hept = heptyl; Oct = octyl.

\*\* API Mass spectral data<sup>8</sup>.

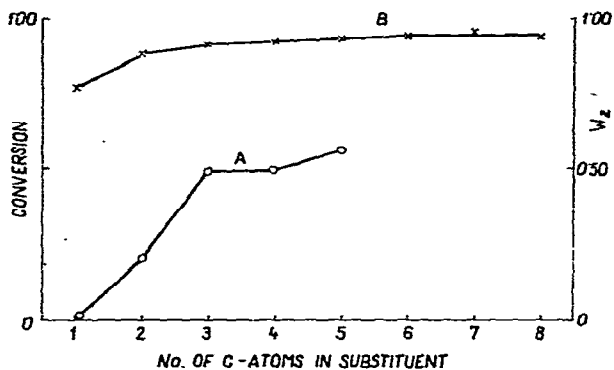


Fig. 1. Relationships between substituent length in mono-*n*-alkylbenzenes and conversion by (A) pyrolysis and (B) electron impact.

benzenes, is shown in Fig. 2. Large differences in the conversion of the isomers in the pyrolytic decomposition are apparent (Fig. 2a), particularly for larger substituents, while the differences in  $W_z$  are slight (Fig. 2b).

The main difference between electron-impact degradation and pyrolysis originates from different C-C bond cleavages depending on the positions of such bonds relative to the aromatic ring. In electron impact the cleavage occurs at the C-C bond in the  $\beta$ -position, while in pyrolysis degradation it occurs at the C-C bond in the  $\gamma$ -

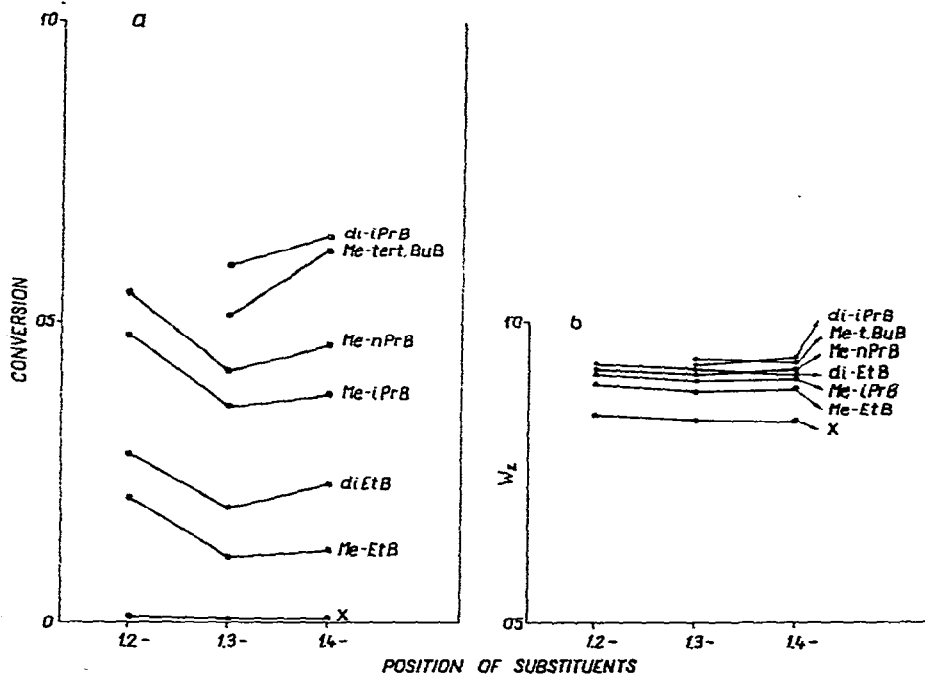


Fig. 2. Relationships between substituent position in dialkylbenzene isomers and the degree of conversion by (a) pyrolysis and (b) electron impact. Abbreviations as in Table I.

position, with or without hydrogen transfer. The amounts of the products obtained in each instance for mono-*n*-alkylbenzenes are given in Fig. 3. The ordinate shows the percentage of toluene as the product of  $\beta$ -cleavage, and also the sum of the amounts of ethylbenzene and styrene produced in the  $\gamma$ -cleavage mechanism. In the case of electron impact the ordinate shows the amounts of the same degradation products obtained by electron impact, calculated from the relationships  $(I_{91} + I_{92})/\Sigma I_f$  ( $\beta$ -cleavage) and  $(I_{104} + I_{105} + I_{106})/\Sigma I_f$  ( $\gamma$ -cleavage), where  $I_{91}$ ,  $I_{92}$ ,  $I_{104}$ ,  $I_{105}$ ,  $I_{106}$  are the intensities of the corresponding masses and  $\Sigma I_f$  is the sum of the intensities of all of the ions in the mass spectrum.

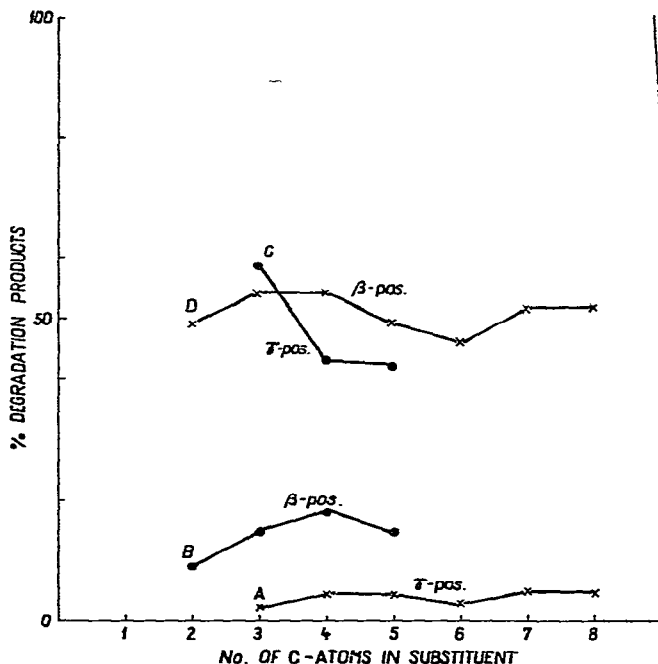


Fig. 3. Relationships between substituent length in mono-*n*-alkylbenzenes and amount of degradation products obtained by splitting of C-C bond in the  $\beta$ - and  $\gamma$ -positions to the aromatic ring. A and B, electron impact; C and D, pyrolysis.

The curves obtained for  $\beta$ -cleavage are initially of the same shape in both instances, while the curves for  $\gamma$ -cleavage are completely different for electron-impact degradation. This type of cleavage remains nearly constant from *n*-propylbenzene to *n*-octylbenzene.

The main products of the pyrolysis of alkylbenzenes and the intensity of the base peak in the mass spectra are often used for identification purposes. Fig. 4 shows the relationship between the amount of the main degradation products and the number of carbon atoms in the substituent in mono-*n*-alkylbenzenes. The intensity of the base peak in the mass spectrum is expressed as a percentage of the total ionization ( $\Sigma_{25}$ ) of monoalkylbenzenes. The amount of the main pyrolysis products decreases regularly with increase in the size of the substituent, but the change in the intensity of the base

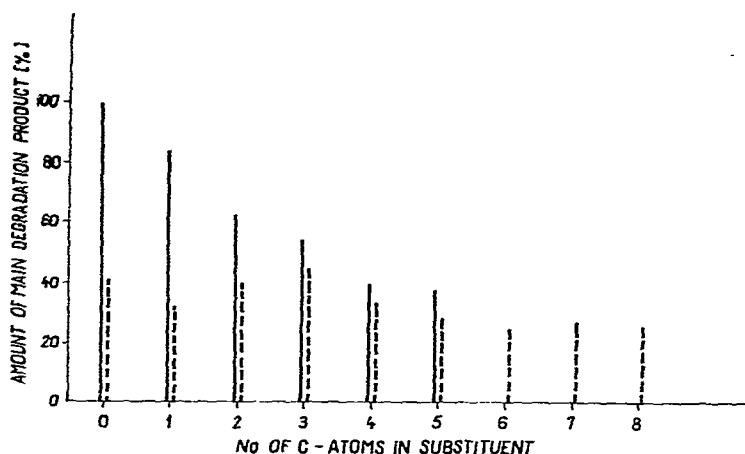


Fig. 4. Relationship between substituent length in mono-*n*-alkylbenzenes and amount of the main degradation product: solid line, pyrolysis; broken line, mass spectrum.

peak in the mass spectrum is not as regular. In general, the intensity of the main degradation product in the mass spectrum for all of the samples investigated was lower than the content of the main pyrolysis product.

These general observations clearly show wider possibilities for the use of pyrolysis gas chromatography in the differentiation of alkylbenzene homologues and closely related isomers, and the di-, tri- and tetraalkylbenzenes are a good example. The mass spectra of many alkylbenzene isomers, such as xylenes, methylethylbenzenes, methyl-*n*-propylbenzenes, methylisopropylbenzenes, diisopropylbenzenes and dimethylethylbenzenes, are so similar that they cannot be used for identification purposes. However, the pyrolysis products from these alkylbenzenes are characteristic of the isomers concerned, especially for those with substitution in the *ortho*-position, and could be used in identification studies. For example, the differences in the characteristic peak intensities in the mass spectra of xylene isomers are only a few per cent, while the production of toluene as the pyrolysis product from *p*-xylene permits a simple identification of this and the other two isomers on the basis of the unidentified characteristic products obtained from *o*- and *m*-xylene.

Methylethylbenzenes show similar mass spectral behaviour. The base peak for all isomers is at *m/e* 105 and the next is the parent peak (*m/e* 120). The values for all of the isomers fall within a very narrow range (0.9% of the base peak) so that this peak cannot be used as the characteristic for individual isomers. On the other hand, the main pyrolysis degradation mechanism of these compounds is dehydrogenation, which gives *o*-, *m*- and *p*-methylstyrenes as pyrolysis products. These compounds could be easily separated chromatographically and measured.

The degradation of all of the methyl-*n*-propylbenzenes by electron impact mainly follows cleavage of the C-C bond in the  $\beta$ -position to the aromatic ring and consequently the differences in their mass spectra are very small. The pyrolysis of methyl-*n*-propylbenzenes strongly affects the cleavage of the C-C bond in the  $\gamma$ -position to the aromatic ring followed by hydrogen transfer reactions for *meta*- and *para*-isomers, which results in equimolar amounts of methane and *m*- and *p*-methylstyrene.

The *ortho*-isomer is degraded through the cleavage of the propyl substituent in the  $\beta$ -position to the aromatic ring, thus yielding *o*-xylene and ethene as products, and also 1-methyl-2-ethylbenzene due to the cleavage of the  $\gamma$ -bond followed by hydrogen transfer. Such distinctive pyrolysis products facilitate the identification of degraded samples.

The mass spectra of methylisopropylbenzenes are difficult to distinguish. The base peak is at  $m/e$  119, originating from cleavage of one of two bonds on the tertiary carbon atom, and the next intense peak is a molecular peak with a sensitivity about one fifth of that of the base peak. In contrast, the pyrogram of 1-methyl-2-isopropylbenzene is easily identified from the large amount of 1-methyl-2-ethylbenzene produced, while 1-methyl-3- and -4-isopropylbenzene give corresponding isomers of methyl- $\alpha$ -methylstyrenes which are easily identified.

The mass spectra of diisopropylbenzenes also do not differ much. The base peak for all isomers is  $(M - 15)^+$  followed by  $(M - 43)^+$  and  $M^+$ . This indicates, however, both the cleavage of methyl from one of the isopropyl groups and the splitting of one isopropyl group, followed by ionization of the molecule. The mechanism of pyrolysis also involves cleavage of a methyl group, but it is accompanied by dehydrogenation, with the result that the main degradation products of *m*- and *p*-diisopropylbenzene are the corresponding vinyl- $\alpha$ -methylstyrenes. The analogous process but free from dehydrogenation gives the corresponding isopropylstyrenes.

As expected, the mass spectra of all six dimethylethylbenzenes are very similar and the identification of these compounds from the mass spectra is difficult. The base peak is  $(M - 15)^+$  formed mainly by splitting the ethyl group of in the  $\beta$ -position to the aromatic ring. The main process in the pyrolysis of these compounds is dehydrogenation, which produces dimethylvinylbenzenes from all isomers except of 1,3-dimethylethylbenzene, which gives 2-methylindane as the main pyrolysis product. This cyclization to yield 2-methylindane is analogous to the *o*-dialkylbenzene reaction. The next characteristic products for all of these compounds, due to the cleavage of ethyl and methyl groups, are 1,2- and 1,3-dimethylbenzenes, ethylbenzene and styrene.

There are instances when it is possible to distinguish one of the three dialkylbenzene isomers by mass spectrometry *e.g.*, diethylbenzenes, methyl-*tert.*-butylbenzenes and trimethylbenzenes.

The appreciably lower intensity of the  $(M - 29)^+$  ion of *p*-diethylbenzene permits its identification, while the main peaks in the mass spectra are of the same intensity for all isomers. However, the pyrograms permit a very easy identification of each isomer. Their pyrolysis gives a very characteristic and pronounced dehydrogenation reaction, producing *m*- and *p*-ethylstyrene as the products from the *meta*- and *para*-isomers and 1-methylindane from the *ortho*-isomer.

With trimethylbenzenes, the mass spectra of 1,2,4- and 1,2,3-trimethylbenzene are very similar but that of 1,3,5-trimethylbenzene has a molecular ion of different intensity (about 10% higher). However, regardless of the same degradation mechanism occurring, the differences in the pyrograms of the trimethylbenzenes are significant. The main process with the 1,2,3-isomer is the splitting of the methyl group in the 3-position, while with the 1,2,4-isomer the 1- and 2-positions are preferentially attacked, giving *m*- and *p*-xylene. The probability of cleaving one methyl group in 1,3,5-trimethylbenzene is equal for all three groups and the main product of pyrolysis is *m*-xylene.

The mechanisms of the degradation of tetramethylbenzenes are the same for electron impact and pyrolysis, both involving cleavage of methyl groups. Consequently their mass spectra are almost identical, while their pyrograms indicate well separated main degradation products and show which methyl group has been split.

#### CONCLUSION

Most of the alkylbenzene homologues and isomers investigated can be identified from the main degradation products of pyrolysis. The mechanisms of the thermal degradation of particular mono-, di- and poly-substituted alkylbenzenes are so different in most instances that the main degradation products are characteristic of the individual isomers concerned. Even when very similar degradation mechanisms occur it is possible to distinguish the isomers on the basis of well resolved pyrolysis fragments.

On the contrary, similar degradation products from alkylbenzene isomers produced by electron impact cannot be distinguished by their mass spectra. Sometimes only particular characteristic fragments can help to distinguish one of several isomers of di- and poly-substituted alkylbenzenes. Hence pyrolysis gas chromatography has considerable advantages over mass spectrometry in the identification of alkylbenzenes.

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