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MECHANISMS OF THE THERMAL DEGRADATION OF ALKYLBENZENES

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SUMMARY

Pyrolysis of more than forty alkylbenzenes was studied and the qualitative and quantitative compositions of the degradation products determined. Pyrolysis was performed in a tubular flow reactor with a gold capillary at 595°. A strong relationship between structure and pyrolysate composition exists even in the case of very closely related isomers. From the results obtained the degradation mechanisms were established for alkylbenzenes.

INTRODUCTION

Our previous paper on the thermal degradation of alkylbenzenes dealt with the identification of alkylbenzenes using light pyrolysis products[1]. It was shown that the degradation products arising from different degradation mechanisms permit the unambiguous identification of all the investigated compounds, even in the case of very closely related isomers.

To establish the mechanisms of the thermal degradation of alkylbenzenes, it is necessary to have more information about the pyrolysate composition than is obtainable through the analysis of the light fraction of the pyrolysate. For these reasons the total composition of the pyrolysis products was determined. The mechanism of thermal degradation of alkylbenzenes in the vapour phase in relation to substituent size, structure and position for more than forty mono- and polysubstituted alkylbenzenes was studied. The results obtained are very interesting with a view to generally accepted opinions about the cleavage of the lateral chains in alkylbenzenes.

EXPERIMENTAL

A tubular flow microreactor with a gold capillary 1119 mm long and 1.2 mm I.D. was used following Cramers and Keulemans[2]. A digital voltmeter and a chromel/alumel thermocouple were used for measuring the reactor temperature. The thermo-

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* Part of Doctoral Thesis.

couple was placed in the core of the reactor. The pyrolyser was connected directly to the gas chromatograph.

A Becker Model 1452 DPF gas chromatograph with flame ionization detector was used (Becker, Delft, The Netherlands).

The light pyrolysis products were analysed in a micropacked glass column using phenyl isocyanate on Porasil C as described earlier[1], but heavier products up to twelve carbon atoms were analysed in a glass capillary column (25.5 m × 0.50 mm I.D.) with silicone rubber GE SE-30.

A Model CRS 11 HB digital readout system (Infotronics, Boulder, Colo., U.S.A.) was used for quantitative interpretation of the chromatograms obtained. A correction factor for peak areas, as described by Dietz[3], was used only for gases and benzene. For all other compounds the peak areas were not corrected, as the flame ionization detector responses to higher hydrocarbons are very close.

Samples were injected with a Hamilton 1-μl syringe with a Chaney adaptor for reproducible injections (Hamilton, Reno, Nev., U.S.A.). Alkylbenzene samples were API standard samples.

Working conditions were as follows: reactor temperature, 595°; reaction time, 20 sec; helium carrier gas flow-rate, 1.47 ml/min; splitting ratio, 1:67; column temperature, 65°; sample size, 0.3 μl.

TABLE I

DEGREE OF CONVERSION OF THE ALKYLBENZENES INVESTIGATED

Pyrolysis temperature, 595°; reaction time, 20 sec.

Compound	Conversion (%)	Compound	Conversion (%)
Monosubstituted			
Toluene	0.6	*sec.*-Butylbenzene	74.3
Ethylbenzene	20.7	*tert.*-Butylbenzene	79.5
n-Propylbenzene	49.1	*n*-Pentylbenzene	56.7
Isopropylbenzene	41.7	*sec.*-Pentylbenzene	74.4
n-Butylbenzene	49.6	*tert.*-Pentylbenzene	95.6
Isobutylbenzene	71.5		
Disubstituted			
1,2-Dimethylbenzene	1.3	1-Methyl-3-*n*-propylbenzene	42.1
1,3-Dimethylbenzene	0.7	1-Methyl-4-*n*-propylbenzene	46.3
1,4-Dimethylbenzene	0.8	1-Methyl-2-isopropylbenzene	47.9
1-Methyl-2-Ethylbenzene	21.1	1-Methyl-3-isopropylbenzene	36.2
1-Methyl-3-Ethylbenzene	10.9	1-Methyl-4-isopropylbenzene	38.0
1-Methyl-4-Ethylbenzene	11.4	1-Methyl-3-*tert.*-butylbenzene	50.7
1,2-Diethylbenzene	27.8	1-Methyl-4-*tert.*-butylbenzene	61.3
1,3-Diethylbenzene	19.7	1,3-Diisopropylbenzene	58.4
1,4-Diethylbenzene	23.3	1,4-Diisopropylbenzene	64.0
1-Methyl-2-*n*-propylbenzene	54.9		
Polysubstituted			
1,2,3-Trimethylbenzene	1.7	1,3-Dimethyl-4-ethylbenzene	26.4
1,2,4-Trimethylbenzene	0.9	1,3-Dimethyl-5-ethylbenzene	11.3
1,3,5-Trimethylbenzene	0.7	1,4-Dimethyl-2-ethylbenzene	21.6
1,3-Dimethyl-2-ethylbenzene	38.5	1,3-Dimethyl-5-*tert.*-butylbenzene	34.2
1,2-Dimethyl-4-ethylbenzene	14.3	1,2,3,4-Tetramethylbenzene	2.2
1,2-Dimethyl-3-ethylbenzene	27.8	1,2,3,5-Tetramethylbenzene	1.8

RESULTS

On the basis of data on the composition of the pyrolysis products the alkyl-benzene conversion is established for the pyrolysis conditions described. The results are given in Table I.

The pyrolysate components were identified by comparison of the retention times (t_R) of pure components, using Kováts' retention indices[4], and by means of the linear relationship between boiling point (T_b) and logarithm of the reduced retention time (log t'_R).

As there was only a very limited number of pure compounds for identification through comparison of t_R values, for most identifications Kováts' retention indices were used. The data obtained from the plot of boiling point $vs.$ log t'_R were also of great help.

Only a few of the products obtained remained unidentified. In general, these compounds appear in small amounts. Their molecular weights are higher than those of the pyrolysed compound, which indicates that these products originate from secondary reactions. Only in two cases were the unidentified compounds the main degradation products, $i.e.$ 1,2-diethylbenzene and 1,3-dimethyl-2-ethylbenzene.

All results obtained are the average values of three or more measurements. Repeatability of the results for n-propylbenzene pyrolysis is shown in Table II.

TABLE II

REPEATABILITY OF CRACKING PATTERNS FOR n-PROPYLBENZENE PYROLYSATES

Component	$\sigma_{abs.}$	$\sigma_{rel.}$ (%)
Gases	±0.033	±0.39
Benzene	0.029	1.67
Toluene	0.098	1.34
Ethylbenzene	0.029	1.27
Styrene	0.055	0.21
Isopropylbenzene	0.029	0.87
Allylbenzene	0.000	0.00
n-Propylbenzene	0.246	0.48
α-Methylstyrene	0.048	0.96
m-Methylstyrene	0.000	0.00
Isobutylbenzene sec.-Butylbenzene }	0.029	0.16
Isoallylbenzene	0.029	1.75
Indene	0.000	0.00

Tables III–V show the pyrolysis products of all the alkylbenzenes investigated. The amounts are given in weight percents. "Trace" means that the component as found is present at less than 0.1 %. A question mark denotes doubtful identification.

DISCUSSION

As with other organic molecules the thermal degradation of alkylbenzenes follows a free radical mechanism, as determined by Rice and coworkers[5-7]. This theory

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TABLE III
COMPOSITION OF MONOSUBSTITUTED ALKYLBENZENE PYROLYSATES

Component	Toluene		Ethylbenzene		n-Propylbenzene		Isopropylbenzene	
	I	%	I	%	I	%	I	%
Methane		16.7		2.7		8.2		6.8
Ethane				1.2		1.7		0.4
Ethene				1.4		6.6		0.5
Propene						0.6		1.7
Benzene	654.8	83.3	654.8	12.0	654.8	3.6	654.8	6.7
Toluene			757.5	9.6	757.6	14.9	757.6	1.7
Ethylbenzene					849.0	4.8	849.1	8.9
Styrene			874.7	62.3	874.6	53.7	874.6	27.8
Isopropylbenzene			910.0	2.4	910.1	0.6		
Allylbenzene					929.3	0.4		
n-Propylbenzene			938.1	3.3				
α-Methylstyrene					963.3	1.1	963.1	43.3
m-Methylstyrene					972.7	1.2		
Isobutylbenzene ⎫ sec.-Butylbenzene ⎭					993.0	0.4		
Isoallylbenzene					1004.2	1.8	1004.2	1.0
Indene					1016.8	0.4	1017.0	0.2
1,4-Diethylbenzene			1035.6	5.1				
?							1036.7	1.0

Component	n-Butylbenzene		Isobutylbenzene		sec.-Butylbenzene		tert.-Butylbenzene	
	I	%	I	%	I	%	I	%
Methane		3.4		5.5		6.5		12.0
Ethane		3.9		0.1		3.0		1.1
Ethene		15.0		1.6		8.9		0.8
Propane		0.2		0.8		1.0		
Propene		6.2		17.0		1.6		3.2
1-Butene				0.2				
Isobutene				2.4				11.9
Benzene	654.8	3.6	654.8	8.6	654.8	4.2	654.8	14.8
Toluene	757.7	17.9	757.6	24.8	757.7	1.3	757.7	3.1
Ethylbenzene	849.1	3.5	849.1	5.3	849.1	7.5	849.1	2.4
Styrene	874.4	39.7	874.8	9.5	874.4	25.7	874.4	5.2
Isopropylbenzene	910.1	0.2	910.1	0.2	910.1	3.1	910.1	3.2
Allylbenzene	929.3	2.2			929.3	0.5		
n-Propylbenzene	938.1	2.4						
α-Methylstyrene	963.1	0.2	963.1	3.9	963.2	21.1	963.1	34.7
m-Methylstyrene			972.7	3.1	972.7	1.5		
Isobutylbenzene ⎫ sec.-Butylbenzene ⎭	993.1	1.0						
Isoallylbenzene	1004.2	0.2	1004.2	12.1	1004.2	4.5	1004.2	2.2
Indene	1016.9	0.4	1016.8	2.0	1017.0	1.2	1016.9	0.5
β-Methylallylbenzene			1022.4	trace				
1,3-Diethylbenzene?					1032.3 ⎫	6.7		
1,4-Diethylbenzene?					1036.7 ⎭		1036.7	0.7
α-Ethylstyrene					1058.4	1.4	1058.4	2.7
α,β-Dimethylstyrene?							1090.7	trace
1,2-Dihydronaphthalene?			1115.0 ⎫	1.5	1115.0 ⎫	1.3	1114.4	0.7
Tetralin?			1119.4 ⎭		1119.4 ⎭		1119.8	0.8
Naphthalene?					1139.4	0.4		

TABLE III *(continued)*

Component	n-Pentylbenzene		sec.-Pentylbenzene		tert.-Pentylbenzene	
	I	%	I	%	I	%
Methane		4.4		5.1		5.1
Ethane		1.7		2.2		4.2
Ethene		20.7		16.1		12.4
Propane				0.4		1.3
Propene		3.1		5.8		1.3
1-Butene		3.9		0.2		
Isobutene						1.3
Benzene	654.8	2.5	654.8	3.7	654.8	6.6
Toluene	757.7	15.0	757.7	0.9	757.6	1.5
Ethylbenzene	849.0	4.8	849.0	6.8	849.1	1.7
Styrene	874.2	37.9	874.2	32.1	874.7	6.5
Isopropylbenzene			910.0	2.8	910.1	5.0
Allylbenzene	929.3	3.0	929.3	0.9		
n-Propylbenzene	938.1	0.7			938.1	0.1
α-Methylstyrene	963.1	1.1	963.1	17.1	963.2	41.3
tert.-Butylbenzene					975.4	2.7
Isobutylbenzene ⎱ sec.-Butylbenzene ⎰			993.1	1.9	993.0	0.2
Isoallylbenzene	1004.2	0.5	1004.1	2.0	1004.2	1.6
Indene	1017.1	0.7	1017.0	0.7	1016.9	0.6
1,4-Diethylbenzene?			1036.7	0.1	1036.7	0.5
β-Ethylstyrene			1058.2	0.1	1058.7	2.1
α,β-Dimethylstyrene?					1090.7	0.2
1,2-Dihydronaphthalene?			1114.2⎱	0.8	1114.8⎱	3.1
Tetralin?			1119.8⎰		1119.7⎰	
Naphthalene?			1139.4	0.3	1139.4	0.7

assumes an approximately first order kinetics and provides a few rules for the prediction of product distribution.

Reaction gas chromatography permits an improved accuracy in determining reaction rates and is more reliable as regards the nature of the products than the classical methods. However, our investigations have shown that it is very important to have available, if possible, the qualitative and quantitative analysis of total volatile degradation products. Thus our previous paper[1] contained other conclusions on the degradation mechanism of particular alkylbenzenes because it was based only on the gaseous hydrocarbon content of the pyrolysate. The present study is, however, made on the basis of the composition of the total volatile part of the pyrolysate.

Of the monosubstituted alkylbenzenes, toluene is thermally the most stable and its conversion at working conditions was very low. In the case of ethylbenzene, the dehydrogenation process occurs to a much higher degree than does C–C bond cleavage. For alkylbenzenes with a straight lateral chain longer than ethyl, the preferred degradation reaction is the cleavage of the bond γ to the phenyl double bond. Accordingly, the main product of n-propylbenzene pyrolysate is styrene. Quite opposite to expectations was the reaction of the C–C bond, breaking in the position β to the phenyl double bond. In this case toluene has to be present in larger amounts. The amounts of styrene and methane in n-propylbenzene pyrolysate are equimolar.

TABLE IV

COMPOSITION OF DISUBSTITUTED ALKYLBENZENE PYROLYSATES

Pyrolyzed compound	Product of pyrolysis	I	%
1,2-Dimethylbenzene	Methane		5.9
	Ethane		0.5
	Ethene		1.3
	Benzene	654.8	trace
	Toluene	757.5	76.9
	?	1035.1	15.4
1-Methyl-2-ethylbenzene	Methane		6.1
	Ethane		0.8
	Ethene		2.6
	Benzene	654.7	trace
	Toluene	757.6	14.2
	Ethylbenzene	849.1	5.2
	1,2-Dimethylbenzene	878.9	13.7
	o-Methylstyrene	990.6	51.7
	Indene	1017.1	3.3
	?	1106.7	2.4
1,2-Diethylbenzene	Methane		4.6
	Ethane		0.8
	Ethene		3.3
	Benzene	654.7	0.7
	Toluene	757.7	1.1
	Ethylbenzene	849.1	10.9
	Styrene	874.7	4.7
	α-Methylstyrene	963.1	5.4
	1-Methyl-2-ethylbenzene	963.8	14.1
	o-Methylstyrene	990.5	trace
	Indene	1016.7	1.1
	1-Methylindane?	1055.1	48.2
	?	1060.5	1.8
	o-Ethylstyrene	1086.4	0.4
	1,2-Dihydronaphthalene?	1113.4 ⎱	1.1
	Tetralin?	1117.5 ⎰	

Pyrolyzed compound	Product of pyrolysis	I	%
1,3-Dimethylbenzene	Methane		5.3
	Ethane		0.7
	Toluene	757.6	73.0
	?	1035.1	21.0
1-Methyl-3-ethylbenzene	Methane		4.0
	Ethane		0.4
	Ethene		1.1
	Toluene	757.7	7.3
	Ethylbenzene	849.1 ⎱	18.3
	1,3-Dimethylbenzene	857.6 ⎰	
	m-Methylstyrene	973.3	68.9
1,3-Diethylbenzene	Methane		4.7
	Ethane		0.6
	Ethene		1.8
	Toluene	757.7	trace
	Ethylbenzene	849.1	10.2
	Styrene	874.7	0.5
	1-Methyl-3-ethylbenzene	948.0	13.7
	m-Methylstyrene	973.2	1.0
	1,3-Divinylbenzene	1063.9	65.5
	?	1085.2	2.0

Pyrolyzed compound	Product of pyrolysis	I	%
1,4-Dimethylbenzene	Methane		11.5
	Ethene		1.0
	Toluene	757.7	87.5
1-Methyl-4-ethylbenzene	Methane		4.1
	Ethane		0.3
	Ethene		0.9
	Toluene	757.7	6.1
	Ethylbenzene	849.1 ⎱	18.4
	1,4-Dimethylbenzene	857.5 ⎰	
	p-Methylstyrene	977.6	70.2
1,4-Diethylbenzene	Methane		4.0
	Ethane		0.5
	Ethene		1.1
	Toluene	757.7	trace
	Ethylbenzene	849.1	8.6
	Styrene	874.7	0.9
	1-Methyl-4-ethylbenzene	948.2	12.9
	p-Methylstyrene	977.6	2.1
	p-Ethylstyrene	1071.7	66.1
	1,4-Divinylbenzene	1095.9	3.8

1-Methyl-2-n-propylbenzene

Product	Index	Yield
Methane		5.1
Ethane		2.3
Ethene		14.4
Propene		0.2
Toluene	757.7	4.0
Ethylbenzene	849.1	0.2
1,2-Dimethylbenzene	878.9	33.5
n-Propylbenzene	938.1	1.1
α-Methylstyrene	963.1	5.3
1-Methyl-2-ethylbenzene	963.9	28.4
o-Methylstyrene	990.6	0.4
2,3-Dihydroindene?	1009.7	0.5
Indene	1017.0	2.2
1,4-Divinylbenzene?	1094.2	0.5
1-Methyl-2-isoallylbenzene?	1116.5	1.5
Naphthalene?	1138.2	0.4

1-Methyl-3-n-propylbenzene

Product	Index	Yield
Methane		7.0
Ethane		2.3
Ethene		6.8
Propene		0.5
Toluene	757.7	3.1
Ethylbenzene	849.1	} 17.6
1,3-Dimethylbenzene	856.8	}
n-Propylbenzene	938.1	
1-Methyl-3-ethylbenzene	948.0	5.2
m-Methylstyrene	973.2	52.7
Isoallylbenzene	1004.2	0.2
1-Methyl-3α-methylstyrene	1062.2	0.7
m-Ethylstyrene	1063.9	0.6
1-Methyl-3-isoallylbenzene	1102.3	1.4
1,2-Dihydronaphthalene?	1114.3	1.2
Naphthalene?	1140.2	0.7

1-Methyl-4-n-propylbenzene

Product	Index	Yield
Methane		7.7
Ethane		3.5
Ethene		9.5
Propene		0.5
Toluene	757.7	2.6
Ethylbenzene	849.3	} 17.3
1,4-Dimethylbenzene	857.1	}
Styrene	874.7	trace
n-Propylbenzene	938.1	1.1
1-Methyl-4-ethylbenzene	948.2	4.1
p-Methylstyrene	977.6	48.6
?	1007.0	0.2
m-Ethylstyrene	1063.9	0.9
p-Ethylstyrene	1071.7	0.5
1,4-Divinylbenzene	1095.9	0.2
1-Methyl-4-isoallylbenzene	1104.2	1.3
Tetralin?	1120.4	0.9
?	1155	1.1

1-Methyl-2-isopropylbenzene

Product	Index	Yield
Methane		8.8
Ethene		0.2
Propene		12.5
Butene		1.7
Toluene	757.7	6.3
Ethylbenzene	849.1	0.2
Styrene	874.5	24.4
Isopropylbenzene	910.1	2.1
α-Methylstyrene	963.1	10.4
1-Methyl-2-ethylbenzene	963.9	28.8
o-Methylstyrene	990.6	1.5

1-Methyl-3-iso-propylbenzene

Product	Index	Yield
Methane		7.2
Ethene		0.4
Propane		0.1
Propene		1.4
Toluene	757.7	5.2
Ethylbenzene	849.1	1.7
Styrene	874.7	0.3
Isopropylbenzene	910.1	3.6
1-Methyl-3-ethylbenzene	948.2	8.0
α-Methylstyrene	963.1	0.8
m-Methylstyrene	973.1	23.3

1-Methyl-4-iso-propylbenzene

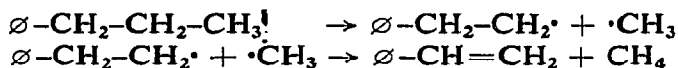| Product	Index	Yield
Methane		7.1
Ethene		0.3
Propene		1.3
Toluene	757.7	5.0
Ethylbenzene	849.2	1.6
Styrene	874.7	0.8
Isopropylbenzene	910.1	3.4
1-Methyl-4-ethylbenzene	948.2	9.2
α-Methylstyrene	963.2	0.8
p-Methylstyrene	977.6	24.7
1-Methyl-4α-methylstyrene	1069.1	44.5

TABLE IV (continued)

Pyrolyzed compound	Product of pyrolysis	I	%	Pyrolyzed compound	Product of pyrolysis	I	%	Product of pyrolysis	I	%
	1-Methyl-3-n-propylbenzene	1031.6	0.4		1-Methyl-3α-methylstyrene	1062.2	45.8	1,4-Divinylbenzene	1095.9	0.5
	1,4-Diethylbenzene	1037.1	0.2		1,3-Divinylbenzene	1085.2	0.8	1-Methyl-4-isoallylbenzene	1104.2	0.8
	1-Methyl-2-n-propylbenzene	1045.8	0.2		1-Methyl-3-isoallylbenzene	1102.3	0.8			
	α,β-Dimethylstyrene	1095.0	0.6		1,2-Dihydronaphthalene?	1113.8	0.3			
	1,2-Dihydronaphthalene?	1114.2 }	1.5		?	1142.9	0.3			
	Tetralin?	1118.5 }								
	Naphthalene?	1140.0	0.2							
1-Methyl-3-tert.-butylbenzene	Methane		10.5	1-Methyl-4-tert.-butylbenzene	Methane		9.3			
	Ethane		0.4		Ethane		0.4			
	Ethene		0.2		Ethene		0.3			
	Propene		1.6		Propene		1.2			
	Isobutene		6.6		Isobutene		4.8			
	Benzene	654.7	0.6		Benzene	654.7	0.7			
	Toluene	757.7	10.6		Toluene	757.7	8.5			
	Ethylbenzene	849.2	2.8		Ethylbenzene	849.1	2.3			
	Styrene	874.7	0.4		Styrene	874.7	0.3			
	Isopropylbenzene	910.1	0.2		Isopropylbenzene	910.1	0.2			
	1-Methyl-3-ethylbenzene	948.3	1.2		1-Methyl-4-ethylbenzene	947.4	1.0			
	α-Methylstyrene	963.1	2.0		α-Methylstyrene	963.1	2.0			
	m-Methylstyrene	973.2	9.8		p-Methylstyrene	977.6	8.5			
	Isoallylbenzene	1004.2	3.5		Isoallylbenzene	1004.2	3.1			
	1-Methyl-3α-methylstyrene	1062.2	39.0		1-Methyl-4α-methylstyrene	1068.3	46.5			
	α,β-Dimethylstyrene?	1093.3	1.4		α,β-Dimethylstyrene?	1092.3	0.7			

Compound	Index	%
1-Methyl-3-isoallylbenzene	1102.3	0.4
1,2-Dihydronaphthalene?	1114.0 }	
Tetralin?	1119.6 }	0.4
?	1128.2	0.6
Naphthalene?	1140.8	4.4
?	1151.9	1.6
?	1166.5	0.4
?	1173.3	1.4

1,3-Diisopropylbenzene	Index	%
Methane		8.0
Ethene		0.5
Propene		1.9
Benzene	654.7	trace
Toluene	757.7	trace
Ethylbenzene	849.1	0.5
Styrene	874.7	0.7
Isopropylbenzene	910.1	5.8
1-Methyl-3-ethylbenzene	948.2	0.3
α-Methylstyrene	963.1	1.4
m-Methylstyrene	973.2	0.3
Isoallylbenzene	1004.2	2.1
1-Methyl-3-allylbenzene	1028.0	0.5
1-Methyl-3α-methylstyrene	1061.0	2.1
1,3-Divinylbenzene	1084.8	11.3
3-Isopropylstyrene?	1117.4	16.3
Naphthalene?	1142.1	2.9
?	1167.4	4.3
3-Vinyl-α-methylstyrene?	1195.8	36.3
?	1248.0	4.8

Compound	Index	%
?	1098.3	1.0
1-Methyl-4-isoallylbenzene	1103.8	0.6
?	1135.7	0.6
?	1154.9	5.2
?	1158.4	1.1
?	1182.9	0.8
?	1189.3	0.9

1,4-Diisopropylbenzene	Index	%
Methane		9.4
Ethane		0.1
Ethene		0.4
Propene		2.0
Benzene	654.7	trace
Toluene	757.7	trace
Ethylbenzene	849.1	0.5
Styrene	874.7	0.9
Isopropylbenzene	910.1	6.1
1-Methyl-4-ethylbenzene	947.6	0.3
α-Methylstyrene	963.1	1.9
p-Methylstyrene	977.5	0.3
Isoallylbenzene	1004.2	1.7
1-Methyl-4-allylbenzene	1033.3	0.6
1-Methyl-4α-methylstyrene	1066.3	2.7
1,4-Divinylbenzene	1093.2	10.8
4-Isopropylstyrene	1136.5	15.8
?	1156.9	3.6
?	1184.8	5.2
4-Vinyl-α-methylstyrene?	1218.5	33.0
?	1277.1	4.7

TABLE V

COMPOSITION OF POLYSUBSTITUTED ALKYLBENZENE PYROLYSATES

Pyrolyzed compound	Product of pyrolysis	I	%
1,2,3-Trimethyl-benzene	Methane		13.6
	Ethane		0.5
	Ethene		0.9
	1,3-Dimethyl-benzene	857.7	25.0
	1,4-Dimethyl-benzene		
	1,2-Dimethyl-benzene	878.9	60.0
1,2,3,4-Tetra-methylbenzene	Methane		15.2
	Ethane		0.5
	Ethene		1.0
	1,2,4-Trimethyl-benzene	974.9	50.0
	1,2,3-Trimethyl-benzene	1005.2	33.3
1,2-Dimethyl-3-ethylbenzene	Methane		5.9
	Ethane		0.3
	Ethene		2.1
	Toluene	757.6	0.7
	Ethylbenzene	849.1	
	1,3-Dimethyl-benzene	857.8	0.4
	Styrene	874.6	
	1,2-Dimethyl-benzene	878.9	13.3
	1-Methyl-3-ethylbenzene	947.2	6.5
	α-Methylstyrene	963.1	5.8
	m-Methylstyrene	973.1	2.9
	o-Methylstyrene	990.6	10.4
	Indene?	1019.8	trace
1,2,4-Trimethyl-benzene	Methane		13.0
	Ethene		0.6
	1,3-Dimethyl-benzene	857.8	51.3
	1,4-Dimethyl-benzene		
	1,2-Dimethyl-benzene	878.9	35.1
1,2,3,5-Tetra-methylbenzene	Methane		13.8
	Ethane		0.3
	Ethene		0.9
	1,3,5-Trimethyl-benzene	952.1	25.0
	1,2,4-Trimethyl-benzene	974.8	60.0
	1,2,3-Trimethyl-benzene	1005.2	trace
1,3-Dimethyl-2-ethylbenzene	Methane		6.8
	Ethane		0.6
	Ethene		4.0
	Toluene	757.6	0.8
	Ethylbenzene	849.1	
	1,3-Dimethyl-benzene	857.8	23.3
	Styrene	874.6	
	1,2-Dimethyl-benzene	878.9	
	1,3,5-Trimethyl-benzene	952.1	9.1
	m-Methylstyrene	974.2	2.1
	o-Methylstyrene	991.4	14.2
	Indene?	1019.8	trace
	2-Methylindane?	1053.4	32.1
1,3,5-Trimethyl-benzene	Methane		12.8
	Ethene		0.6
	1,3-Dimethyl-benzene	857.8	86.6
1,3-Dimethyl-4-ethylbenzene	Methane		8.9
	Ethane		0.6
	Ethene		2.2
	Toluene	757.7	0.4
	Ethylbenzene	849.1	16.3
	1,3-Dimethyl-benzene	857.7	
	1,4-Dimethyl-benzene		
	1-Methyl-4-ethylbenzene	947.2	4.9
	α-Methylstyrene	963.2	3.8
	m-Methylstyrene	975.0	15.5
	1,3-Dimethyl-4-vinylbenzene	1079.8	45.1

1,2-Dimethyl-3-vinylbenzene

Product		
Tetralin?	1097.1	45.0
Naphthalene?	1117.9	3.2
?	1139.8	trace
?	1311.0	1.0
?	1317.0	2.5

1,2-Dimethyl-4-ethylbenzene

Product		
Methane		4.7
Ethane		0.2
Ethene		0.7
Styrene	874.6 }	5.6
1,2-Dimethyl-benzene	878.9 }	
1-Methyl-3-ethylbenzene	948.2 }	10.4
1-Methyl-4-ethylbenzene	948.2 }	
m-Methylstyrene	974.0	14.7
1,2-Dimethyl-4-vinylbenzene	1099.8	63.7

1,3-Dimethyl-5-tert.-butylbenzene

Product		
Methane		19.9
Ethane		0.4
Ethene		0.3
Propene		2.1
Isobutene		8.3
Toluene	757.7	1.1
1,3-Dimethyl-benzene	857.8	14.7
1-Methyl-3-ethylbenzene	948.2	1.9
α-Methylstyrene	963.1	3.0
m-Methylstyrene	973.1	1.1
Isoallylbenzene	1004.2	1.1
?	1038.3	1.7

1,3-Dimethyl-4-vinylbenzene

Product		
?	1081.0	0.5
?	1092.4	trace
Tetralin?	1117.9	4.7
?	1125.2	0.5
Naphthalene?	1142.7	1.0
?	1153.9	0.3

1,4-Dimethyl-2-ethylbenzene

Product		
Methane		5.8
Ethane		0.4
Ethene		1.7
Toluene	757.7	0.5
Ethylbenzene	849.1 }	13.0
1,3-Dimethyl-benzene	}	
1,4-Dimethyl-benzene	857.8 }	
1-Methyl-3-ethylbenzene	947.3	8.3
α-Methylstyrene	963.0	3.7
m-Methylstyrene	973.2	15.7
1,4-Dimethyl-2-vinylbenzene	1075.8	49.0
?	1107.9	0.5
1,2-Dihydro-naphthalene?	1114.5	1.4

1,2-Dihydro-naphthalene?

Product		
	1114.5	0.4
Naphthalene?	1139.8	1.9

1,3-Dimethyl-5-ethylbenzene

Product		
Methane		4.5
Ethane		0.2
Ethene		0.9
Ethylbenzene	849.1 }	6.2
1,3-Dimethyl-benzene	}	
1-Methyl-3-ethylbenzene	857.8 }	
1-Methyl-3-ethylbenzene	947.5	7.0
1,3,5-Trimethyl-benzene	}	
m-Methylstyrene	951.8	14.2
1,3-Dimethyl-5-vinylbenzene	974.2	trace
	1072.9	67.0

TABLE V (continued)

Pyrolyzed compound	Product of pyrolysis	I	%	Pyrolyzed compound	Product of pyrolysis	I	%	Pyrolyzed compound	Product of pyrolysis	I	%
	1-Methyl-3α-methylstyrene	1061.0	4.6								
	?	1065.0	12.9								
	1-Methyl-3-tert.-butylbenzene	1067.5	5.0								
	?	1095.3	10.9								
	?	1181.5	2.0								
	?	1228.2	3.4								
	?	1235.6	0.9								
	?	1244.9	1.5								
	?	1267.3	3.2								

$$\varnothing-CH_2-CH_2-CH_3 \rightarrow \varnothing-CH_2-CH_2\cdot + \cdot CH_3$$
$$\varnothing-CH_2-CH_2\cdot + \cdot CH_3 \rightarrow \varnothing-CH=CH_2 + CH_4$$

The same result regarding the position of the C–C bond which preferably undergoes degradation is found for *n*-butylbenzene, *n*-pentylbenzene and *sec.*-pentylbenzene. The main degradation product of these monosubstituted alkylbenzenes was styrene. These observations are in agreement with the results of the pyrolysis of dodecylbenzene published by Derge[8], who also found styrene as the main product in the pyrolysate.

Alkylbenzenes with the lateral group connected to a phenyl group through a tertiary carbon atom follow different paths of degradation than alkylbenzenes with normal chain substituents.

Degradation of isopropylbenzene gives equimolar amounts of styrene and ethylbenzene, on one side and α-methylstyrene on the other. Evidently, cleavage of the C–C bond in the position β is present. Both processes, the breaking of C–C bonds and the dehydrogenation, are of the same intensity. Due to the lower strength of the C–C bond between the phenyl group and the tertiary carbon atom, benzene is found as the degradation product.

Breaking of the C–C bond in the position β to the phenyl double bond occurred also in the case of isobutylbenzene degradation. The next reactions, of equal intensity, are the breaking of the C–C bond in the position α to the phenyl group, and cleavage of a methyl group from the tertiary carbon atom. The last reaction gives isoallyl-benzene:

$$\varnothing-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \rightarrow \varnothing-CH_2-\underset{\underset{\cdot}{|}}{CH}-CH_3 + \cdot CH_3$$
$$\downarrow + R\cdot$$
$$\varnothing-CH=CH-CH_3 + RH$$
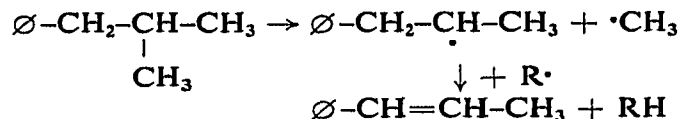
The main degradation product resulting from the pyrolysis of *sec.*-butylbenzene is styrene:

$$\varnothing-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \rightarrow \varnothing-\underset{\underset{CH_3}{|}}{CH}\cdot + \cdot CH_2-CH_3$$
$$\downarrow + R\cdot$$
$$\varnothing-\underset{\underset{CH_2}{||}}{CH} + RH$$
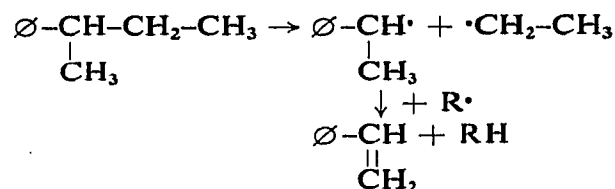
This reaction is followed by a γ-bond cleavage, as indicated by the appearance of α-methylstyrene. The molar ratio of these two products is 1:0.60.

Degradation of *tert.*-butylbenzene and *tert.*-pentylbenzene develops as follows:

$$\varnothing-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \rightarrow \varnothing-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot + \cdot CH_3$$
$$\downarrow + R\cdot$$
$$\varnothing-\underset{\underset{CH_2}{||}}{\overset{\overset{CH_3}{|}}{C}} + RH$$
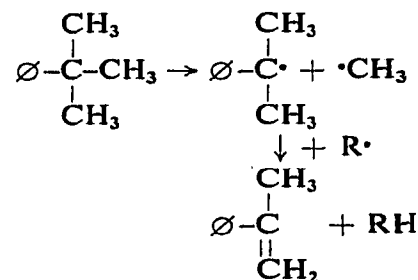
and, as indicated, gives α-methylstyrene as the main degradation product. The C–C bond between a quaternary carbon and a phenyl group is weaker, thus resulting in a quite remarkable amount of benzene in the degradation products.

In the case of dialkylbenzenes the most stable are xylenes. The small amount of toluene appears as the degradation product.

Methylethylbenzenes are subject to a strong dehydrogenation process and produce methylstyrene isomers. The *meta* and *para* isomers of methylethylbenzene give nearly the same amount of methylstyrene products, while the *ortho* isomer gives about 25 % less *o*-methylstyrene isomer. The difference in the degradation mechanism of methylethylbenzenes becomes evident through the presence of a cyclic product in the pyrolysate of the *ortho* isomer. This is indene, whose origin could be explained by an easier transfer reaction in the case of substituents in neighbouring positions.

A more complicated degradation mechanism is found for diethylbenzenes. Isomers of *m*- and *p*-diethylbenzene show a characteristic and marked dehydrogenation of one ethyl group, resulting in *m*- and *p*-ethylstyrenes. The cleavage of the methyl or ethyl group is more pronounced in the *meta* isomer. *o*-Diethylbenzene has a different degradation path. Its main degradation product is certainly 1-methylindane, based on retention index ($I_{65°}^{SE-30} = 1053.5$) and boiling point value ($T_b = 187°$).

Very strong cleavage in the position γ to the phenyl double bond is found as well as hydrogen transfer for *m*- and *p*-methyl-*n*-propylbenzenes. The degradation products contain equimolar amounts of methane and *m*- and *p*-methylstyrenes. The characteristic behaviour of the *ortho* isomer in producing *o*-xylene and ethylene could be explained by C–C bond cleavage in the propyl substituent β to the phenyl group. All three isomers give small and identical amounts of methylisoallylbenzene isomers.

Very pronounced degradation of *m*- and *p*-methylisopropylbenzenes results in methyl-α-methylstyrenes as distinctive degradation products:
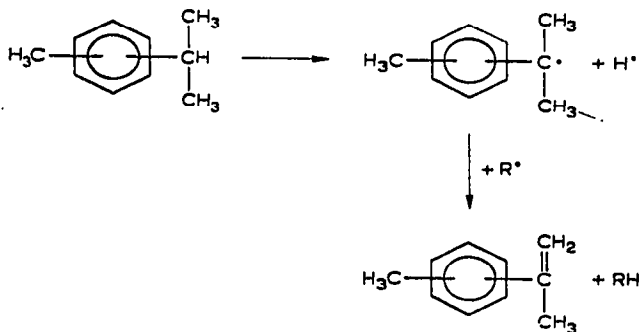

This type of dialkylbenzene also shows a different behaviour of the *ortho* isomer, forming *o*-methylethylbenzene and styrene in equivalent amounts.

We have investigated two methyl-*tert.*-butylbenzene isomers only. They have closely related degradation mechanisms. The main process is the splitting off of a methyl group in the *tert.*-butyl substituent, giving *m*- and *p*-methyl-α-methylstyrenes.
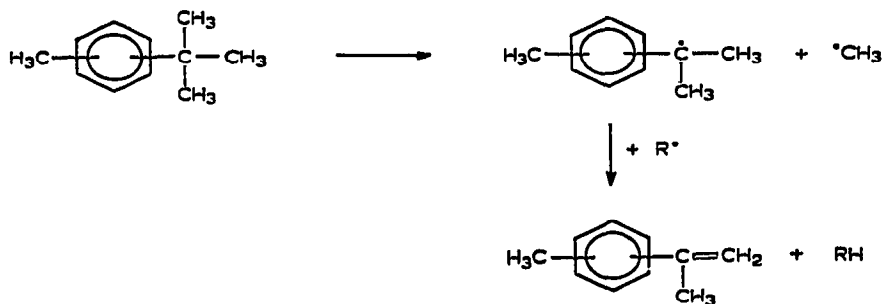
Since in the molecule of these compounds the C–C bond between the phenyl and *tert.*-butyl groups is very weak, they further degradate resulting in the formation of toluene.
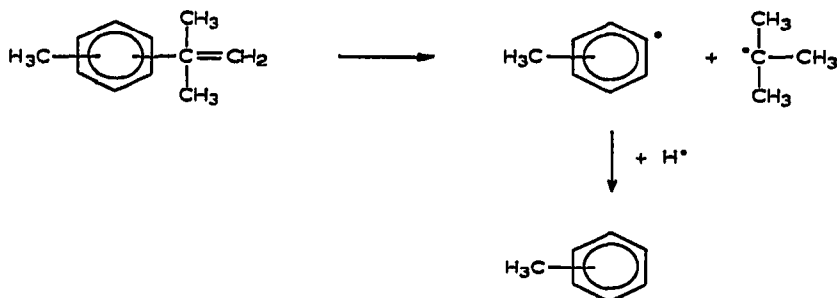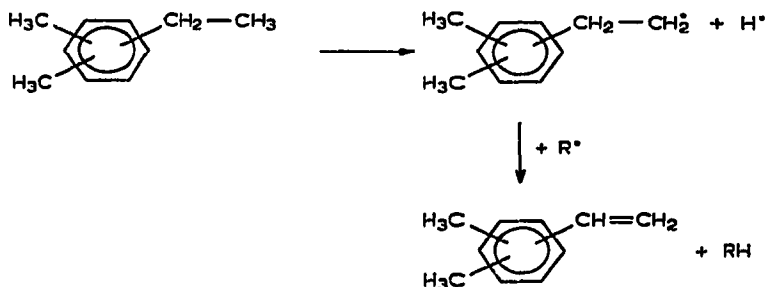
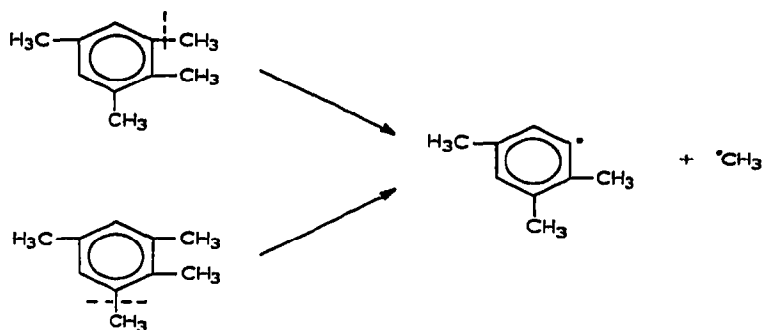Toluene and isobutene are present in equimolar concentrations.

Diisopropylbenzenes are relatively large molecules and undergo extensive degradation. The main degradation products found in the pyrolysate are vinyl-α-methylstyrene and isopropylstyrene. Methyl group splitting in the isopropyl substituents is extensive and is the cause of the formation of diethylbenzenes.

Trisubstituted benzenes generally show a higher degree of conversion than disubstituted ones. A simpler degradation mechanism includes the cleavage of methyl groups from phenyl. In the case of 1,2,3-isomers, *o*-xylene is the main degradation product, thus suggesting the cleavage of substituents in positions 1 or 3. A different situation arises in the case of 1,2,4-isomers, the degradation products of which contain 1,3- and 1,4-dimethylbenzenes and only a small amount of *o*-xylene.

With the exception of 1,3-dimethyl-2-ethylbenzene, all dimethylethylbenzene pyrolysates contain unsaturated derivatives; this can be explained by a dehydrogenation reaction of the ethyl substituent.

The subsequent reaction is cleavage of a methyl group from the benzene ring, resulting in a variety of components containing methyl and ethyl or methyl and vinyl groups.

As already mentioned, 1,3-dimethyl-2-ethylbenzene behaves in a different way. The degree of conversion is higher and the main degradation product is thought to be 2-methylindane. (Since the pure substance, or other reliable information, was lacking, identification was possible only by means of boiling point and retention index.) A great difference is evident in the interaction between neighbouring groups when the ethyl group is placed between two methyl groups or when the ethyl group is in the neighbourhood of two methyl groups in *ortho* position.

Cleavage of the methyl group from the benzene ring also occurs in the degradation of 1,3-dimethyl-2-ethylbenzene, as with other dimethylethylbenzene isomers. It is interesting also to point out the distinctive variety of degradation products in the case of 1,3-dimethyl-2-ethylbenzene in contrast with other dimethylethylbenzene isomers.

The mechanism of the very intensive degradation of 1,3-dimethyl-5-*tert.*-butylbenzene can be explained as follows:

$$
H_3C-\underset{CH_3}{\underset{|}{\underset{\bigcirc}{}}}-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \longrightarrow H_3C-\underset{CH_3}{\underset{\bigcirc}{}}\cdot + \cdot\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3
$$

$$\downarrow + H^\cdot \qquad\qquad \downarrow + R^\cdot$$

$$
H_3C-\underset{CH_3}{\underset{\bigcirc}{}} \qquad\qquad \underset{CH_3}{\overset{CH_2}{\underset{|}{\overset{||}{C}}}}-CH_3 + RH
$$

The amounts of *m*-xylene and isobutene evolved are equimolar. Some higher-molecular-weight compounds are found amongst the degradation products; these are very probably unsaturated and cyclic compounds derived from the parent molecule.

Only two tetrasubstituted methylbenzenes, *i.e.* 1,2,3,4- and 1,2,3,5-tetramethylbenzene, were investigated. 1,2,4,5-Tetramethylbenzene has a solid structure and is therefore inconvenient for pyrolysis in a flow microreactor. The degradation mechanism of 1,2,3,4-tetramethylbenzene shows a tendency to form other isomers of trimethylbenzenes, rather than the isomer with vicinal substitution, owing to the lower stability of the latter.

1,2,4-Trimethylbenzene forms a great part of the degradation products of

1,2,3,5-tetramethylbenzene and could evolve via two degradation processes:

About one third of the molecules are degraded by the splitting off of the methyl group in position 2, giving 1,3,5-trimethylbenzene.

CONCLUSION

Thermal degradation of alkylbenzenes with normal lateral chains shows a distinctive breaking of the C–C bond in the position γ to the phenyl double bond. This differs from the generally accepted opinion that the C–C bond β to the phenyl double bond preferably undergoes cleavage.

A branched lateral chain causes on the one hand splitting off of the whole substituent from the phenyl group and, on the other hand, splitting off of a methyl group from a tertiary carbon atom. This process is distinctly present in the case of quaternary carbon atoms in a lateral chain.

Isomers of polysubstituted alkylbenzenes show typical behaviour in the case of vicinal substituents. A greater degree of degradation and a very complex pyrolysate composition is observed in the case of o-dialkylbenzenes, rather than in the case of the *meta* and *para* isomers. A lower thermal stability of polysubstituted alkylbenzenes with substituents in a vicinal position also results in their degradation into more stable isomers.

ACKNOWLEDGEMENT

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