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MASS SPECTROMETRIC STUDIES ON POLYPHENYLS
PART I
THE MASS SPECTRA OF DIPHENYL, THE TERPHENYLS AND QUATERPHENYLS

by

W. BEYRICH, A. COPET and S. FACCHETTI

1965

ORGEL PROGRAM

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Analytical and Inorganic Chemistry Service

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1. INTRODUCTION

In connection with the ORGEL-Project (1), the investigation of the thermal and radiolytic behaviour of the terphenyls as possible reactor coolants is part of the Research Program of Euratom (2).

The application of the mass spectrometric technique to the analysis of polyphenyls as well as to studies of the fragmentation processes occurring on these compounds under electron bombardment is therefore of interest.

Until now, only little information exists in literature on the mass spectra of polyphenyls (3-6) and, to our knowledge, especially no complete data on the different isomers have been published. This is probably due to the fact that products of sufficient purity were not available or that the mass spectrometers used did not allow the handling of these low volatile compounds.

2. PURITY OF SAMPLES

The samples of diphenyl (Φ_2), the 3 terphenyls (o-, m-, and p- Φ_3) and the 6 quaterphenyl isomers (o-o-, o-m-, o-p-, m-m-, m-p-, p-p- Φ_4) used for the measurements have been produced and purified by the Organic Chemistry Section of Euratom, Ispra, and by the Company S.E.R.A.I., Bruxelles (7), under Euratom contract. The purity of these compounds has been checked by gaschromatography (8) and thin layer chromatography (9). With the exception of the p-p-quaterphenyl, the purity was 99 % or better (see table 1). An additional check on the purity of the compounds by taking the mass spectra at electron energies of less than 20 eV was made. There were also no peaks visible which could be attributed to impurities.

TABLE 1
Purity of Samples

Compound	Impurity
Diphenyl	less than 0.01 %
o- Terphenyl	less than 0.01 %
m- Terphenyl	less than 0.01 % (*)
p- Terphenyl	less than 0.2 %
o-o- Quaterphenyl	less than 0.01 %
o-m- Quaterphenyl	less than 0.01 %
o-p- Quaterphenyl	less than 1.0 %
m-m-Quaterphenyl	about 1.0 %
m-p- Quaterphenyl	less than 0.1 %
p-p- Quaterphenyl	about 2.0 %

3. EXPERIMENTAL

For the measurements a conventional single focusing 60° magnetic sector field mass spectrometer type Atlas CH4 has been used. The instrument was equipped with the Atlas high temperature inlet system, which allows direct introduction of the sample in the solid state.

This inlet system has been operated at a temperature of 260°C, the ion source at 300°C. An accelerating voltage of 3 kV and an electron beam current of 33×10^{-6} amps have been used. The spectra have been taken at different electron energies between 10 and 70 eV (**).

The total ion current could be measured by a collector assembly located between the ion source and the magnetic sector and was in the order of 1×10^{-10} amps. However, attempts to determine the ratio of the total ion current to the amount of sample introduced gave no results of satisfactory reproducibility. This is very probably caused by insufficient cooling of the sample in the vacuum lock leading to a loss of sample during the introduction.

The magnetic scanning of the spectra has been started 10 minutes after opening of the valve to the ion source. During this time, the total ion current reached a stable value.

The occurrence of a peak at $m/e = 44$ with changing intensity indicated the formation of CO_2 by combustion of a small part of the sample. By adding a large amount of oxygen to the sample it could be shown that even if the CO_2-peak increases to a value 10 to 100 times higher than normally observed, the relative intensities of the peaks formed by fragments of the polyphenyl molecules are not influenced.

The pumping out time for p-p-quaterphenyl (the least volatile product measured, see table 2) was about one hour to reach 0.5 % of the original ion current intensity.

(*) It should be noted, that the m-terphenyl is free of p-terphenyl.
(**) Only the 50 and 70 eV spectra are discussed in this report.

TABLE 2

Approximate Values for Melting and Boiling Point of Polyphenyls (*)

Compound	M.P. °C	B.P. °C
Diphenyl	69	255
o- Terphenyl	56	332
m- Terphenyl	87	364
p- Terphenyl	213	385
o-o- Quaterphenyl	118	420
o-m- Quaterphenyl	90	
o-p- Quaterphenyl	119	
m-m-Quaterphenyl	86	471
m-p- Quaterphenyl	166	
p-p- Quaterphenyl	318	520

4. RESULTS

The mass spectra taken with a nominal electron energy of 50 and 70 eV are shown in table 3.

Columns 1 and 2 give, respectively, the number of C-atoms contained in the fragment and the mass-to-charge ratio m/e.

In the following columns, the relative intensities for $m/e > 25$ and the type of peak are shown. Relative intensities of less than 10 % are given with 2 decimals, the last figure is made round to 0 or 5. For the type of peak, the abbreviations d = « double charged ion », t = « triple charged ion », p = « parent peak », i = « isotope peak » and r = « rearrangement » have been used. Metastable peaks have not been indicated.

The relative intensities at $m/e = 28$ have not been reported in the spectra, as these values are rather uncertain because of the corrections for background and carbon dioxide contribution (see page 4) which had to be applied. By high resolution mass spectrometry with an A.E.I. model MS 9 instrument it could be shown that the $C_2H_4^+$-ion exists and that the value of its relative intensity is in general between those found for the peaks at $m/e = 26$ and $m/e = 27$.

5. DISCUSSION

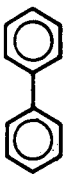
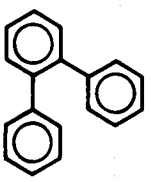
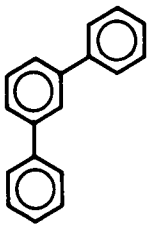
5.1. General

All the mass spectra reported show a very intense peak at the molecular mass as this is in general the case for aromatic compounds (10). The great number of peaks occurring at half mass units indicates the formation of many double charged ions which will certainly contribute also to the intensities of the peaks at integral mass numbers below one half of the molecular weights. Especially the peaks at one half of the molecular masses are mainly due to double charged molecular ions (**) and small peaks at $m/e = 76.7$ in the 70 eV-mass spectra of m- and p-terphenyl indicate even the occurrence of triple charged

(*) These values have been taken mainly from the « Organic Coolant Databook », Monsanto Chemical Company, St. Louis, Technical Publication No. AT-1, 1958.

(**) The amount of double charged molecular ions contributing to the peak p/2 can be estimated by the intensity of the double charged isotopic peak of the molecule, occurring at a half mass unit.

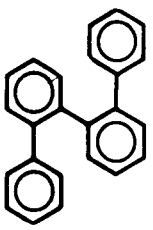
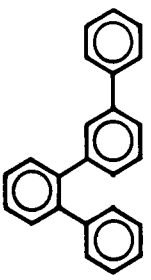
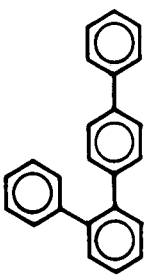
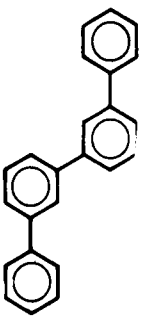
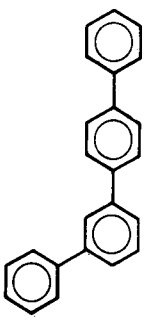
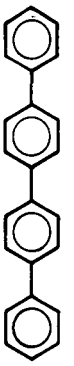
TABLE 3 - MASS

Number of C-Atoms	m/e	DIPHENYL Relative Intensities 70 eV	50 eV	Type of Peak	o-TERPHENYL Relative Intensities 70 eV	50 eV	m-TERPHENYL Relative Intensities 70 eV	50 eV	p-TERPHENYL Relative Intensities 70 eV	50 eV	Type of Peak
	26	0.2	0.1		0.2	0.2	0.1		0.15	0.1	
2 C	27	0.55	0.4	r	0.65	0.4	0.25	0.1	0.35	0.15	r
	28 (*)										
	37	0.1									
3 C	38	0.25			0.15				0.1		
	39	2.15	1.95		2.5	1.9	2.85	0.55	1.4	0.9	
	49	0.1									
	50	2.8	2.05		1.55	0.85	0.65	0.3	0.95	0.45	
4 C	51	6.0	5.4		3.75	3.1	1.65	1.05	2.45	1.65	
	51.5	0.1		d							
	52	1.2	1.25		0.8	0.75	0.4	0.3	0.6	0.45	
	53	0.1	0.1	i,r?	0.1	0.1			0.1		
	61	0.3			0.1						
	62	1.2	0.75		0.9	0.35	0.35	0.1	0.55	0.15	
	62.5	0.1		d							
	63	4.95	3.95		3.05	2.15	1.25	0.7	1.85	1.15	
5 C	63.5	0.3	0.2	d							
	64	6.2	5.3		0.3	0.25	0.15	0.1	0.2	0.15	
	64.5	0.55	0.5	d							
	65	0.75	0.8		0.7	0.8	0.35	0.35	0.6	0.6	
	69.5	0.3	0.2	d	0.1		0.1		0.1		d
	73	0.15									
	74	2.0	1.45		1.6	0.75	0.65	0.25	0.85	0.35	
	74.5	0.1		d							
	75	3.1	2.65		2.75	1.6	1.15	0.6	1.55	0.85	
	75.5	1.75	1.25	d	0.15		0.1		0.15		d
	76	17.8	15.6		2.5	2.25	1.75	1.25	2.5	1.85	
	76.5	3.05	2.55	d	0.1	0.1	0.1	0.1	0.2	0.15	d
6 C	76.7						0.1		0.15		t
	77	8.65	8.75		1.85	2.45	1.35	1.25	1.85	1.9	
	77.5	0.7	0.7	d,i							
	78	1.0	1.05	i,r	0.35	0.5	0.35	0.3	0.45	0.5	i,r
	81.5				0.45	0.25	0.25	0.1	0.3	0.1	d
	82				0.1	0.1	0.1		0.1		
	82.5				0.25	0.25	0.2	0.1	0.2	0.15	d
	83				0.1	0.1					

(*) see page 5

SPECTRA OF POLYPHENYLS

o-o- QUATERPHENYL Relative Intensities		o-m- QUATERPHENYL Relative Intensities		o-p- QUATERPHENYL Relative Intensities		m-m- QUATERPHENYL Relative Intensities		m-p- QUATERPHENYL Relative Intensities		p-p- QUATERPHENYL Relative Intensities		Type of Peak	m/e
70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		
						0.2	0.15	0.2	0.15				26
						0.2		0.15				r	27
													28 (*)
													37
													38
0.9		0.6				0.75	0.4	0.65	0.3	0.2			39
													49
0.4		0.3		0.2		0.4	0.15	0.4	0.15	0.1			50
2.15	1.0	1.55	0.65	1.05	0.55	1.2	0.5	1.15	0.5	0.55	0.2		51
													51.5
						0.25	0.1	0.25	0.1				52
													53
													61
						0.15		0.15					62
													62.5
1.2		1.0	0.2	0.65	0.2	0.8	0.3	0.75	0.25	0.35			63
													63.5
						0.1		0.1					64
													64.5
		0.15		0.2		0.25	0.2	0.25	0.2				65
													69.5
													73
0.35		0.25		0.2		0.3	0.1	0.3	0.1	0.1			74
													74.5
0.7		0.6		0.5		0.6	0.2	0.55	0.2	0.25			75
													75.5
0.5		0.45	0.2	0.35	0.2	0.55	0.25	0.55	0.25	0.2			76
													76.5
													76.7
2.0	1.75	2.0	1.85	1.45	1.65	1.35	1.1	1.3	1.05	0.75	0.65		77
													77.5
0.65	0.65	0.45	0.45	0.5	0.5	0.25	0.2	0.35	0.3	0.1	0.1	i,r	78
													81.5
													82
													82.5
													83

Number of C-Atoms	m/e	DIPHENYL Relative Intensities 70 eV	50 eV	Type of Peak	o-TERPHENYL Relative Intensities 70 eV	50 eV	m-TERPHENYL Relative Intensities 70 eV	50 eV	p-TERPHENYL Relative Intensities 70 eV	50 eV	Type of Peak
	85	0.15									
	86	0.55	0.4		0.65	0.25	0.25	0.1	0.3	0.1	
	86.5								0.15		d
	87	0.85	0.85		1.9	0.9	0.75	0.3	0.95	0.4	
	87.5				0.3		0.1		0.15		d
	88	0.35	0.4		4.85	3.35	2.15	1.2	2.55	1.45	
	88.5				0.7	0.45	0.3	0.2	0.4	0.2	d
	89	1.15	1.25		1.7	2.1	1.5	1.35	2.25	2.1	
7 C	89.5				0.15	0.15	0.15	0.15	0.25	0.2	d
	90	0.1	0.1	i,r?	0.1	0.1			0.1	0.1	
	91	0.3	0.3	r	0.15	0.25	0.4	0.45	0.7	0.8	
	92								0.1	0.1	
	93				0.1						
	93.5				0.7	0.35	0.25	0.1	0.3	0.1	d
	94				0.55	0.45	0.25	0.15	0.3	0.15	
	94.5				4.05	4.4	1.2	0.9	1.2	0.95	d
	95				0.7	0.75	0.25	0.25	0.3	0.25	
	95.5								0.1		d
	98	0.55	0.35		0.6	0.2	0.25		0.3	0.1	
	99	0.4	0.35		0.9	0.4	0.35	0.15	0.4	0.15	
	99.5				0.55	0.2	0.15		0.2		d
	100	0.25	0.25		5.0	2.9	1.55	0.75	1.6	0.75	
	100.5				1.65	1.25	0.6	0.4	0.6		d
	101	0.75	0.85		14.4	17.0	5.45	4.5	5.45	4.45	
	101.5				2.95	3.35	1.1	0.9	1.15	0.95	d
8 C	102	2.4	2.6		1.6	2.25	1.5	1.45	2.0	2.2	
	103	0.3	0.35	i,r?	0.1	0.2	0.15	0.2	0.25	0.25	
	105.5				0.2	0.1					d
	106				0.45	0.35	0.15	0.1	0.1		
	106.5				2.15	2.15	0.6	0.45	0.55	0.4	d
	107				1.5	1.8	0.35	0.3	0.3	0.25	
	107.5				8.85	11.8	1.55	1.45	0.85	0.8	d
	108				1.6	2.15	0.25	0.25	0.15	0.15	
	108.5				0.1	0.15					d
	110	0.1			0.2				0.1		
	111	0.1	0.1		0.4	0.15	0.15		0.2		
	111.5				0.4	0.15	0.1				d
	112				2.9	1.6	0.6	0.3	0.5	0.2	
	112.5				2.2	1.7	0.5	0.3	0.4	0.25	d
	113	0.45	0.55		14.0	14.4	3.9	3.1	3.7	2.95	
	113.5				5.0	5.7	1.35	1.1	1.25	1.05	d
	114	0.3	0.3		16.1	21.5	2.4	2.5	2.1	1.95	
9 C	114.5				5.6	7.65	0.7	0.65	0.55	0.5	d
	115	3.9	4.1		6.1	9.05	9.95	10.6	14.7	15.9	
	115.5				0.85	1.3	1.6	1.7	2.4	2.65	d,i
	116	0.35	0.35	i	0.15	0.25	0.3	0.35	0.45	0.5	d,i
	118										
	118.5										
	119										
	119.5										
	120										
	120.5										

o-o- QUATERPHENYL		o-m- QUATERPHENYL		o-p- QUATERPHENYL		m-m- QUATERPHENYL		m-p- QUATERPHENYL		p-p- QUATERPHENYL			
Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Type of Peak	m/e
70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		
													85
						0.1		0.1					86
													86.5
0.45		0.3		0.25		0.3		0.3	0.1	0.15			87
													87.5
0.35		0.3		0.25		0.35		0.4	0.1	0.15			88
													88.5
0.4		0.4	0.15	0.25	0.25	0.4	0.3	0.4	0.25	0.15	0.1		89
													89.5
													90
3.0	3.1	4.1	4.6	4.35	5.7	0.4	0.45	0.4	0.45	0.15	0.2		91
			0.15	0.35	0.3			0.1					92
													93
								0.1				d	93.5
													94
						0.2		0.2				d	94.5
													95
													95.5
						0.1		0.1					98
						0.15		0.15					99
													99.5
0.7		0.75		0.65		0.45		0.45		0.3			100
								0.1				d	100.5
0.7	0.35	0.9	0.3	0.8	0.35	0.75	0.4	0.8	0.4	0.65	0.3		101
								0.1				d	101.5
0.4	0.35	0.55	0.4	0.55	0.45	0.9	0.7	1.1	0.8	1.2	0.85		102
0.4	0.4	0.4	0.55	0.5	0.65	0.4	0.45	0.4	0.45	0.2	0.25		103
													105.5
													106
0.25		0.3		0.3		0.3		0.35		0.2		d	106.5
						0.1							107
						0.1		0.15				d	107.5
													108
													108.5
													110
						0.1							111
													111.5
0.8		0.65		0.65		0.4		0.35		0.2			112
		0.2		0.2		0.15		0.2				d	112.5
2.35	0.8	2.75	0.9	2.25	0.95	1.4	0.55	1.4	0.55	1.35	0.5		113
0.4		0.3		0.3		0.3	0.1	0.3	0.1	0.15		d	113.5
0.4	0.3	0.4	0.3	0.4	0.35	0.3	0.2	0.3	0.25	0.2			114
													114.5
1.0	1.05	0.9	1.0	0.8	0.95	0.95	0.95	1.0	1.0	0.8	0.9		115
													115.5
							0.1	0.1				i	116
						0.1		0.1					118
0.7		0.7		0.65		0.4		0.4		0.25		d	118.5
0.35		0.3		0.25		0.2	0.1	0.25	0.1	0.1			119
1.4	0.7	1.55	0.8	1.35	0.85	0.8	0.4	0.8	0.45	0.8	0.4	d	119.5
0.3		0.25		0.2		0.25	0.15	0.3	0.15	0.15			120
						0.1		0.1	0.1			d	120.5

Number of C-Atoms	m/e	DIPHENYL Relative Intensities 70 eV	50 eV	Type of Peak	o-TERPHENYL Relative Intensities 70 eV	50 eV	m-TERPHENYL Relative Intensities 70 eV	50 eV	p-TERPHENYL Relative Intensities 70 eV	50 eV	Type of Peak
	124										
	124.5										
	125	0.3	0.3		0.25	0.3	0.15	0.15	0.2	0.15	
	125.5										
	126	2.25	2.5		1.3	1.8	0.95	1.0	1.05	1.1	
	126.5										
	127	2.55	2.8		0.65	1.05	0.75	0.8	0.9	1.0	
10 C	128	3.25	3.2		0.4	0.7	1.85	1.9	2.35	2.55	
	129	0.3	0.3	i			0.2	0.2	0.25	0.25	i
	130.5										
	131										
	131.5										
	132										
	132.5										
	133										
	133.5										
	136.5										
	137				0.2	0.2	0.1		0.1		
	137.5										
	138				0.15	0.15			0.1		
11 C	138.5										
	139	1.55	1.65		0.95	1.35	0.65	0.65	0.8	0.8	
	139.5										
	140	0.2	0.15	i	0.1	0.15			0.1	0.1	i
	143										
	143.5										
	144										
	144.5										
	145										
	145.5										
	146										
	149	0.3	0.35		0.25	0.3	0.15	0.15	0.15	0.15	
	149.5										
	150	1.9	2.3		1.6	2.1	1.05	1.05	1.1	1.1	
12 C	150.5										
	151	7.1	7.95		2.1	3.2	2.45	2.65	2.7	3.0	
	151.5										
	152	23.5	25.8		2.7	4.45	4.6	5.1	4.9	5.65	
	152.5										
	153	31.6	31.3		0.5	0.85	1.9	1.95	2.05	2.25	
	153.5										
	154	100.0	100.0	p		0.15	0.4	0.45	0.55	0.6	i,r
	155	12.9	12.9	i							
	156	0.7	0.7	i							

o-o- QUATERPHENYL		o-m- QUATERPHENYL		o-p- QUATERPHENYL		m-m- QUATERPHENYL		m-p- QUATERPHENYL		p-p- QUATERPHENYL			
Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Type of Peak	m/e
70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		
0.5		0.3		0.35		0.2		0.2					124
0.3		0.2		0.2				0.15				d	124.5
2.9	0.65	2.95	0.7	2.5	0.8	1.1	0.35	1.1	0.35	1.05	0.25		125
0.5		0.4		0.45		0.25	0.1	0.3	0.1	0.15		d	125.5
2.4	1.55	3.1	2.0	2.75	2.15	1.8	1.25	1.85	1.25	1.85	1.35		126
0.25		0.3		0.35	0.25	0.3	0.15	0.3	0.2	0.2	0.1	d	126.5
0.35		0.4	0.4	0.4	0.45	0.65	0.6	0.7	0.7	0.65	0.65		127
0.6	0.55	0.4	0.4	0.35	0.4	1.0	1.1	1.1	1.2	1.0	1.1		128
						0.1	0.1	0.1	0.15				129
0.7		0.55		0.55		0.3		0.25		0.1		d	130.5
0.7		0.55		0.5		0.3	0.1	0.25	0.1	0.15			131
4.75	2.4	4.1	2.2	3.4	2.15	1.4	0.75	1.35	0.7	1.25	0.65	d	131.5
1.8	0.95	1.4	0.9	1.25	0.85	0.6	0.4	0.6	0.4	0.5	0.3		132
1.85	1.3	1.55	1.25	1.45	1.3	0.85	0.65	0.9	0.7	0.9	0.7	d	132.5
1.05	0.8	0.5	0.55	0.65	0.65	0.3	0.25	0.35	0.3	0.3	0.15		133
						0.2	0.2	0.3	0.25	0.25	0.2	d	133.5
						0.1		0.1				d	136.5
2.65	0.35	2.25	0.35	1.95	0.4	0.8	0.2	0.7	0.2	0.55			137
1.0	0.3	0.75	0.25	0.7	0.25	0.4	0.2	0.4	0.2	0.2		d	137.5
10.0	6.6	8.3	5.3	7.05	5.25	2.7	1.6	2.65	1.55	2.75	1.75		138
2.85	1.9	2.45	1.55	2.2	1.65	0.95	0.6	0.95	0.65	0.9	0.5	d	138.5
3.3	2.9	3.1	2.75	2.9	2.85	1.25	1.0	1.3	1.1	1.35	1.15		139
0.4	0.25	0.35	0.3	0.45	0.4	0.25	0.2	0.3	0.25	0.1	0.1	d	139.5
						0.25	0.2	0.35	0.35	0.35	0.25		140
0.65		0.3	0.15	0.2		0.15		0.1					143
4.2	2.0	2.9	1.45	2.25	1.3	0.7	0.4	0.6	0.35	0.4	0.15	d	143.5
3.35	2.2	2.0	1.45	1.7	1.3	0.55	0.4	0.5	0.4	0.35	0.2		144
14.1	11.5	10.8	8.9	9.1	8.4	2.35	1.95	2.15	1.8	2.15	1.9	d	144.5
17.4	15.3	9.0	7.95	7.8	7.8	1.45	1.25	1.3	1.2	1.25	1.15		145
5.45	4.8	4.35	4.0	3.85	3.9	0.5	0.45	0.45	0.45	0.3	0.25	d	145.5
0.6	0.35	0.5	0.55	0.5	0.5								146
1.05		0.65		0.55		0.3	0.1	0.3	0.1	0.15			149
0.6		0.35		0.35		0.2		0.2	0.1			d	149.5
6.4	2.8	5.9	2.85	5.1	3.0	2.05	1.1	1.9	1.05	1.9	1.0		150
2.35	1.1	2.2	1.2	1.95	1.3	0.8	0.5	0.8	0.5	0.7	0.4	d	150.5
8.8	6.85	8.8	6.9	8.05	7.3	3.55	3.05	3.5	3.0	3.75	3.25		151
3.05	2.4	2.9	2.25	2.7	2.45	0.95	0.75	0.95	0.8	1.0	0.8	d	151.5
5.0	4.8	4.9	4.95	4.8	5.75	4.4	4.5	4.2	4.5	4.5	4.6		152
1.05	0.85	0.95	0.8	1.1	1.2	0.7	0.65	0.8	0.75	0.85	0.8	d	152.5
4.0	4.2	4.35	4.55	4.5	5.4	18.5	19.7	19.3	20.5	26.2	26.9		153
0.75	0.65	0.75	0.7	0.9	1.05	4.55	4.85	4.7	5.15	6.5	6.65	d,i	153.5
				0.15	0.2	0.9	0.95	0.9	1.0	1.05	1.15	d,i	154
													155
													156

Number of C-Atoms	m/e	DIPHENYL Relative Intensities 70 eV	50 eV	Type of Peak	o-TERPHENYL Relative Intensities 70 eV	50 eV	m-TERPHENYL Relative Intensities 70 eV	50 eV	p-TERPHENYL Relative Intensities 70 eV	50 eV	Type of Peak
	161				0.1	0.1					
	162				0.25	0.25	0.1		0.1	0.1	
	163				1.45	2.0	0.5	0.5	0.55	0.5	
13 C	164				0.65	1.0	0.2	0.2	0.2	0.2	
	165				3.0	4.4	0.9	0.95	0.8	0.85	
	166				0.4	0.6	0.1	0.15	0.1	0.15	i
	167										
	174				0.55	0.6	0.2	0.15	0.2	0.15	
	175				0.65	0.9	0.25	0.25	0.3	0.25	
14 C	176				1.8	2.65	0.9	0.9	0.95	1.0	
	177				0.5	0.75	0.25	0.3	0.3	0.3	
	178				0.65	1.0	0.35	0.4	0.4	0.45	
	179				0.1	0.15		0.1	0.1	0.1	i,r?
	186				0.15	0.15					
	187				1.1	1.4	0.4	0.4	0.4	0.4	
	188				0.65	0.9	0.25	0.3	0.25	0.25	
15 C	189				2.6	3.9	1.6	1.75	1.6	1.7	
	190				0.5	0.75	0.35	0.35	0.35	0.35	
	191				0.25	0.35	0.3	0.35	0.35	0.4	i,r?
	192										
	198				0.25	0.2	0.1		0.1		
	199				0.6	0.6	0.2	0.2	0.2	0.2	
	200				3.25	3.65	1.3	1.4	1.25	1.35	
16 C	201				3.0	3.55	1.3	1.4	1.2	1.25	
	202				11.0	11.9	4.95	5.5	4.8	5.1	
	203				4.2	4.3	1.9	2.0	1.7	1.8	
	204				0.6	0.55	0.4	0.4	0.4	0.4	i
	211				0.2	0.2		0.1			
	212				0.2	0.25	0.1	0.1		0.1	
	213				2.1	2.35	0.9	1.0	0.8	0.9	
17 C	214				0.75	0.8	0.35	0.35	0.3	0.3	
	215				27.6	27.6	3.8	3.9	2.6	2.7	
	216				5.2	5.15	0.7	0.7	0.45	0.5	
	217				0.4	0.45					i
	222				0.1	0.1					
	223				0.35	0.4	0.1	0.1	0.1	0.1	
	224				1.9	2.35	0.75	0.9	0.65	0.8	
	225				2.7	3.45	1.1	1.35	1.0	1.1	
	226				14.7	18.1	6.35	7.65	5.65	6.85	
18 C	227				11.1	13.0	5.55	6.2	4.85	5.4	
	228				30.2	33.7	13.8	15.2	11.9	12.9	
	229				53.9	57.3	13.5	10.8	7.05	7.5	
	230				100.0	100.0	100.0	100.0	100.0	100.0	p
	231				18.6	18.8	19.5	19.5	19.4	19.4	i
	232				1.65	1.65	1.8	1.8	1.8	1.8	i
	233				0.1	0.1	0.1	0.1	0.1	0.1	i

o-o-QUATERPHENYL		o-m-QUATERPHENYL		o-p-QUATERPHENYL		m-m-QUATERPHENYL		m-p-QUATERPHENYL		p-p-QUATERPHENYL			
Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Type of Peak	m/e
70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		
													161
													162
0.75	0.45	0.5	0.4	0.55	0.4	0.4	0.25	0.35	0.25	0.2			163
	0.2	0.2	0.2	0.2	0.2	0.15	0.15	0.15	0.15				164
3.2	3.35	3.25	3.6	3.15	3.7	0.95	1.05	0.85	0.95	0.65	0.7		165
	0.25	0.25	0.3	0.25	0.25	0.15	0.15	0.1	0.15			i	166
						0.1	0.1	0.1	0.1			r?	167
		0.2		0.1		0.1		0.1					174
		0.2		0.2		0.15	0.15	0.15	0.15				175
0.7	0.75	0.8	0.75	0.9	0.9	0.65	0.6	0.7	0.65	0.55	0.45		176
		0.2	0.15	0.2	0.25	0.25	0.25	0.3	0.3	0.15	0.15		177
1.7	1.75	0.8	0.8	0.7	0.85	0.5	0.55	0.6	0.65	0.6	0.65		178
						0.1	0.1	0.1	0.1			i	179
													186
0.5		0.35	0.25	0.4	0.25	0.25	0.15	0.3	0.15	0.15			187
		0.25		0.2	0.2	0.15	0.15	0.2	0.15				188
1.2	1.15	1.15	1.25	1.25	1.3	1.0	1.05	0.9	1.1	0.9	0.95		189
		0.2	0.15	0.15	0.2	0.2	0.25	0.2	0.25	0.15	0.1		190
0.9	0.85	0.85	0.85	0.85	0.85	0.5	0.55	0.6	0.65	0.5	0.5		191
								0.1	0.1			i	192
													198
						0.1		0.1					199
1.65	1.35	1.2	1.1	1.2	1.1	0.75	0.6	0.7	0.6	0.4	0.35		200
1.15	1.15	0.9	1.0	0.95	1.0	0.65	0.6	0.6	0.6	0.35	0.35		201
4.85	5.4	4.05	4.5	3.95	4.5	2.25	2.4	2.1	2.35	1.85	2.05		202
1.45	1.6	1.55	1.85	1.85	2.1	1.05	1.1	0.95	1.1	0.75	0.8		203
		0.3	0.35	0.25	0.3	0.4	0.4	0.4	0.45	0.3	0.3		204
						0.1		0.1					211
													212
0.7	0.8	0.7	0.7	0.8	0.75	0.45	0.4	0.45	0.4	0.25	0.2		213
			0.15	0.15	0.2	0.1	0.1	0.1	0.1				214
14.2	14.5	18.5	18.4	23.7	24.3	1.05	1.1	0.9	0.95	0.6	0.55		215
2.3	2.45	3.2	3.25	4.25	4.35	0.2	0.2	0.15	0.15			i	216
				0.25	0.2							i	217
													222
								0.1					223
1.25	1.0	0.85	0.75	0.9	0.75	0.5	0.4	0.5	0.4	0.3	0.15		224
1.45	1.65	1.05	1.2	1.05	1.15	0.7	0.7	0.65	0.65	0.4	0.35		225
9.75	11.15	8.2	9.1	8.05	9.25	3.9	4.35	3.65	4.1	3.1	3.6		226
5.85	6.6	4.3	4.8	4.1	4.65	2.3	2.5	2.15	2.4	1.8	2.0		227
20.0	21.7	12.7	13.4	11.8	2.7	4.0	4.4	3.7	4.15	3.2	3.65		228
23.1	23.5	13.0	13.2	11.5	1.9	2.05	2.15	1.7	1.8	1.25	1.3		229
3.85	4.0	2.5	2.55	2.2	2.25	0.45	0.45	0.35	0.4	0.3	0.4	i	230
													231
													232
													233

Number of C-Atoms	m/e	DIPHENYL Relative Intensities 70 eV	50 eV	Type of Peak	o-TERPHENYL Relative Intensities 70 eV	50 eV	m-TERPHENYL Relative Intensities 70 eV	50 eV	p-TERPHENYL Relative Intensities 70 eV	50 eV	Type of Peak
	237										
19 C	239										
	240										
	241										
	248										
	249										
	250										
20 C	251										
	252										
	253										
	254										
	261										
	262										
	263										
21 C	264										
	265										
	266										
	267										
	273										
	274										
	275										
22 C	276										
	277										
	278										
	279										
	280										
	287										
	288										
23 C	289										
	290										
	291										
	292										
	298										
	299										
	300										
	301										
	302										
24 C	303										
	304										
	305										
	306										
	307										
	308										
	309										

o-o-QUATERPHENYL		o-m-QUATERPHENYL		o-p-QUATERPHENYL		m-m-QUATERPHENYL		m-p-QUATERPHENYL		p-p-QUATERPHENYL			
Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Relative Intensities		Type of Peak	m/e
70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		
	0.35	0.25	0.3	0.35	0.25	0.2	0.15	0.2	0.15				237
1.4	1.7	1.35	1.55	1.4	1.45	0.6	0.65	0.55	0.6	0.3	0.3		239
	0.25		0.2	0.25	0.25	0.15	0.15	0.15	0.15				240
0.65	0.85	0.6	0.65	0.5	0.55	0.1	0.15	0.1	0.1				241
				0.15		0.1		0.1					248
						0.1		0.1					249
0.95	1.1	0.85	0.95	0.85	0.85	0.5	0.4	0.45	0.4	0.25	0.5		250
	0.3		0.25	0.2	0.25	0.15	0.15	0.2	0.15				251
1.9	2.25	1.8	2.0	1.45	1.65	0.8	0.85	0.75	0.75	0.5	0.45		252
0.45	0.65	0.35	0.5	0.4	0.4	0.2	0.25	0.2	0.25				253
					0.2			0.1	0.1				254
	0.25			0.2	0.2	0.1	0.1	0.1	0.1				261
							0.1	0.1	0.1				262
1.4	1.75	1.2	1.4	1.15	1.25	0.6	0.8	0.7	0.7	0.4	0.45		263
0.25	0.4	0.25	0.35	0.3	0.35	0.25	0.3	0.25	0.25	0.1	0.1		264
3.55	3.85	3.05	3.3	1.65	1.85	0.65	0.7	0.55	0.6	0.3	0.35		265
0.45	0.7	0.4	0.55	0.25	0.3	0.15	0.2	0.15	0.15				266
							0.1	0.1	0.1				267
						0.15	0.1	0.15	0.15				273
0.9	1.0	0.85	0.95	0.85	0.9	0.55	0.45	0.5	0.45	0.2	0.2		274
0.85	1.0	0.75	0.9	0.65	0.85	0.45	0.4	0.4	0.4	0.15	0.2		275
5.75	6.55	5.4	6.0	4.75	5.5	2.15	2.35	1.9	2.15	1.4	1.7		276
3.75	4.2	3.35	3.7	2.75	3.15	1.25	1.4	1.1	1.25	0.75	0.85		277
2.8	3.1	2.5	2.7	1.95	2.2	1.0	1.1	0.9	1.05	0.65	0.7		278
1.35	1.55	1.05	1.15	0.85	1.0	0.4	0.45	0.35	0.4	0.1	0.15		279
						0.1	0.15	0.1	0.15				280
0.7	1.0	0.65	0.9	0.65	0.85	0.4	0.45	0.35	0.4	0.15	0.15		287
1.2	1.5	1.2	1.4	1.0	1.2	0.45	0.5	0.4	0.45	0.15	0.15		288
16.2	18.2	17.4	19.1	16.6	18.3	5.5	6.05	4.7	5.2	3.8	4.3		289
9.5	10.2	9.85	10.6	9.4	10.2	2.4	2.65	2.0	2.15	1.45	1.6		290
10.1	10.5	12.8	13.0	10.4	10.8	1.45	1.55	1.2	1.3	0.8	0.85		291
1.95	2.05	2.65	2.75	2.1	2.1	0.3	0.3	0.25	0.25	0.1			292
	0.45	0.25	0.25	0.25	0.25	0.2	0.1	0.2	0.15				298
	0.45	0.25	0.3	0.25	0.35	0.2	0.2	0.2	0.25				299
2.8	3.6	2.75	3.7	2.6	3.45	1.25	1.5	1.2	1.45	0.8	1.05		300
2.1	2.8	2.25	2.95	2.1	2.85	1.15	1.4	1.15	1.35	0.7	0.95		301
8.25	10.5	9.55	11.8	9.2	11.6	3.5	4.3	3.3	4.05	2.7	3.4		302
7.4	9.15	8.4	9.8	7.7	9.05	3.1	3.6	2.9	3.35	2.35	2.75		303
6.65	7.65	8.1	9.25	8.35	10.6	2.9	3.35	2.85	3.3	2.4	2.85		304
17.6	18.0	19.3	19.4	16.0	16.6	2.0	2.1	1.7	1.85	1.2	1.35		305
100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	p	306
25.7	26.1	26.2	26.2	26.2	26.5	26.3	26.1	26.1	26.1	26.2	26.2	i	307
3.05	2.9	2.95	3.05	3.05	3.05	3.35	3.3	3.3	3.3	3.2	3.15	i	308
						0.25	0.25	0.25	0.25	0.15	0.1	i	309

molecular ions, which are very seldom observed in the mass spectra of organic compounds (*).

For the following discussion of the spectra, it is important to note that for each family of polyphenyl isomers with the same number of rings, equal total ionization (defined as the total ion current produced per unit sample pressure in the inlet system) can be assumed. This is justified as theoretical considerations have shown that the relative total ionization cross-sections of molecules are given by the sum of the cross-sections of their constituent atoms (11).

The calculations on the following chapters are always based on the 70 eV-spectra.

5.2. Total Fragmentation

The ratio of the intensity I(P) of single charged ions having molecular mass to the total ionization T.I. (see table 4) shows much smaller values for the isomers containing an ortho-bond than for the others. This means that the ortho-structure has the lowest stability against bombardment with electrons of 70 eV nominal energy. The differences in the values for the other isomers are rather small but indicate a slightly higher stability for para- than for meta-structures.

For these calculations I(P) has been defined as $I(P) = \sum_{k=o}^{2} I(p+k)_{corr.}$ where p is the mass number of the parent peak and the index « corr. » indicates, that the peak intensities have been corrected for isotopic contributions of fragment peaks. T.I. represents the sum over the intensities of all peaks in the spectrum (**).

The ratio I(P)/T.I. calculated in this way does not represent exactly the ratio of all positive ions of the intact molecule to the total number of ions formed, as cleavage of a C-C-bond does not necessarily lead to a fragment of lower mass and as double charged molecular ions are considered like fragment ions.

5.3. Hydrogen Loss Processes

The ratio of the intensity I(P−1) of the (P−1)-ions (loss of one hydrogen atom from the molecule) as well as the ratio of the sum of the intensities $\sum_{n=1}^{8} I(P-n)$ of all ions of the type (P−n) with n = 1, 2 . . . 8 (loss of one to eight hydrogen atoms from the molecule) to the total ionization T.I. is also shown in table 4 (***). The amount of fragments formed by the loss of more than eight hydrogen atoms and also the formation of H_2^+-ions are negligible and therefore have been omitted.

The values show for the terphenyls a considerably decreasing probability for hydrogen loss processes in the order ortho-, meta-, para-terphenyl with remarkable high values for the ortho-terphenyl. For the quaterphenyl isomers, two groups can easily be distinguished: compounds containing at least one ortho-bond and those containing only meta- and para-bonds. The probability for hydrogen loss processes is much higher for the first group of isomers than for the second. Furthermore, meta-bonds seem to favour hydrogen loss more than para-bonds (****).

(*) In the case of quaterphenyls, eventually formed triple charged molecular ions would overlap with fragment ions at m/e = 102.

(**) This definition of the total ionization can be used, as here and in the following part of the discussion only ratios are considered which are given by ion intensities of the same spectrum.

(***) Double charged ions are not taken into consideration. The symbol (P-n) is used in the same sense as P under 5.2 to describe all ions of a certain type, this means with the same number of carbon and hydrogen atoms, independent from the isotopic composition.

(****) It should be mentioned again that these hydrogen loss processes may be combined with a rupture of one C-C-bond of each ring or even with rearrangement processes.

TABLE 4
Total Fragmentation and Hydrogen Loss of Polyphenyls

Compound	I (P)/T.I. × 100	I (P−1)/T.I. × 100	$\sum_{n=1}^{8}$ I (P−n)/T.I. × 100
Diphenyl	40.8	12.1	25.6
o- Terphenyl	23.8	12.7	27.3
m- Terphenyl	46.0	5.13	17.0
p- Terphenyl	46.5	2.26	12.6
o-o- Quaterphenyl	25.8	4.35	10.4
o-m- Quaterphenyl	27.4	5.03	12.5
o-p- Quaterphenyl	29.0	4.25	11.8
m-m-Quaterphenyl	48.0	0.65	5.50
m-p- Quaterphenyl	48.7	0.51	5.24
p-p- Quaterphenyl	52.7	0.35	4.24

5.4. Carbon Loss Processes

In order to compare the behaviour of the different isomers as far as carbon loss processes are concerned, « group » ionizations have been calculated. These group ionizations $I(-C_m)$ (*) with $m = 0, 1, 2 \ldots$ have been defined as the sum of the intensities of all ions formed by the loss of fragments containing 0, 1, 2 . . . carbon atoms (**).

5.4.1. Terphenyls

The group ionizations $I(-C_m)$ for $m = 0, 1, 2 \ldots 8$ in percent of the total ionization T.I. are shown in Fig. 1 for the three terphenyl isomers. The high similarity in the behaviour of meta- and para-terphenyl and the very different behaviour for ortho-terphenyl is remarkable and leads to the assumption that in the case of ortho-terphenyl rather different steps are involved in the fragmentation process. The conception of a relatively small interaction between the rings in meta- and para-position would explain the similarity between the curves of these isomers and the dotted line, which represents the group ionizations for diphenyl. The fact that $I(-C_2)$ has the highest value of the three group ionizations $I(-C_1)$, $I(-C_2)$ and $I(-C_3)$ is also found in the mass spectrum of benzene (***) and may be considered to be characteristic for the opening of a ring which is in the case of para-terphenyl in end position.

For benzene and diphenyl, it is the ion of the type (p−26) — loss of C_2H_2 — which gives the main contribution to the group ionization $I(-C_2)$, for meta- and para-terphenyl it is the ion of the type (p−28), corresponding to the loss of a C_2H_4-group.

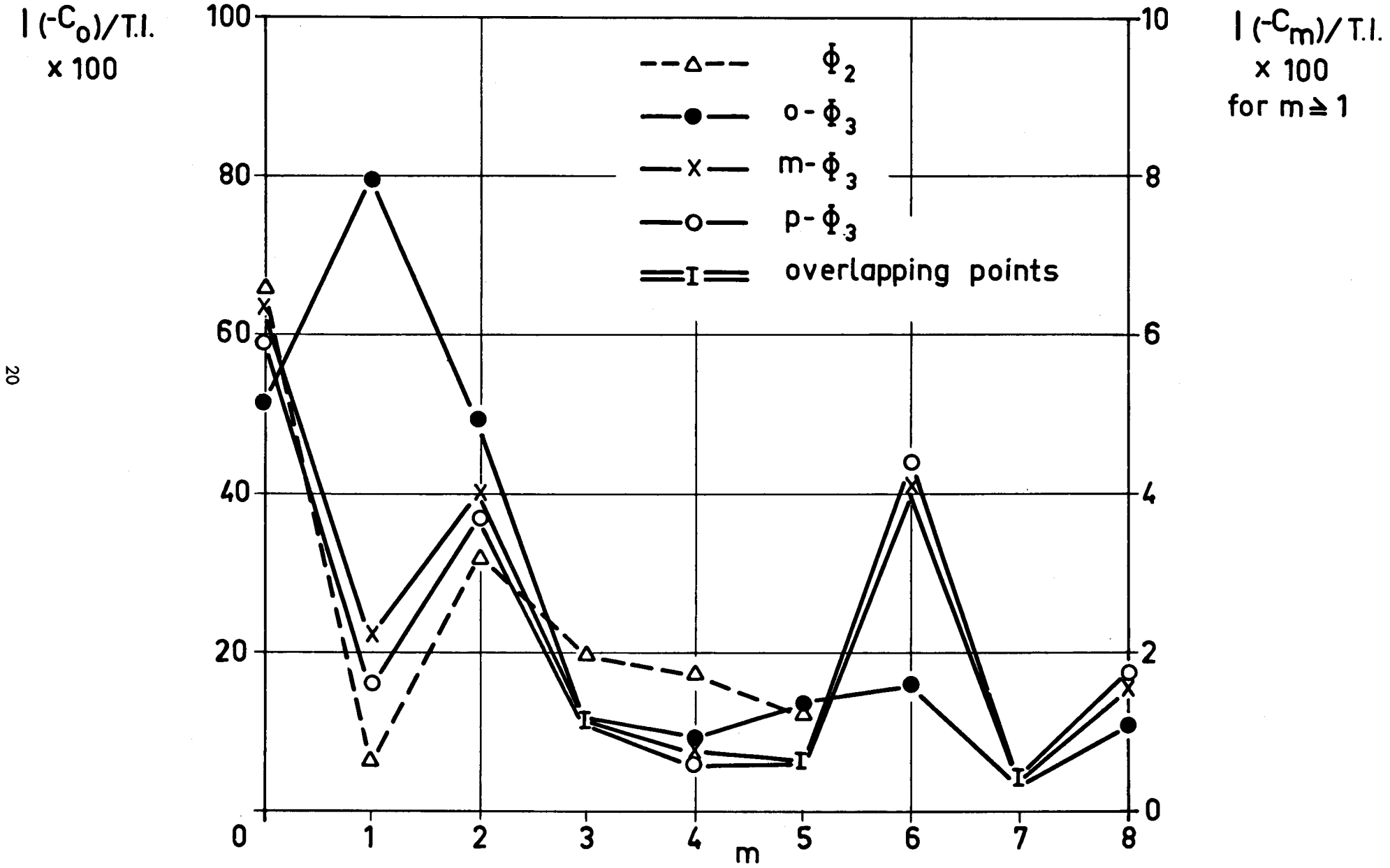
Contrary to this, the curve for ortho-terphenyl shows a steady decrease from $I(-C_1)$ to $I(-C_3)$ and a much less marked maximum at $I(-C_6)$ compared to the meta- and para-isomer. This suggests that in this case also other fragmentation processes may gain

(*) In the symbol $I(-C_m)$ the minus sign shall indicate that C_m describes the number of carbon atoms lost by fragmentation.

(**) Because of the rather disturbing contribution of double charged ions, group ionizations for $m > 8$ in the case of the terphenyls and for $m > 11$ in the case of the quaterphenyls are not considered. The given values are therefore not directly representative for the total amount of (charged plus uncharged) fragments with a certain number of carbon atoms.

(***) See e. g. API-spectrum No. 1591.

Fig.1 Relative Group Ionizations $I(-C_m)/T.I.$ for Diphenyl and the Terphenyls



importance, e.g. opening of the ring in center position or rearrangement of the molecule forming an alkyl-phenantrene structure caused by the higher interaction of the two phenyl rings in ortho-position are possible processes which could be assumed.

In the case of the ortho-terphenyl, ions of the type $(p-15)$ — loss of CH_3 — and $(p-28)$ — loss of C_2H_4 — give the main contribution to the group ionizations $I(-C_1)$ and $I(-C_2)$.

5.4.2. Quaterphenyls

The group ionizations for the 6 quaterphenyl isomers are shown in fig. 2.

Again, a remarkable difference exists between the curves for the isomers containing ortho-bonds compared to the others. The general shape of the curves for $7 \leqslant m \leqslant 11$ is similar to the corresponding part $(1 \leqslant m \leqslant 5)$ for the terphenyls (fig. 1). This may indicate that after the loss of a C_6H_5-group, the remaining fragment of a quaterphenyl behaves similar to the corresponding terphenyl. On the other hand, the addition of the fourth ring changes remarkably the group ionizations for dissociation processes leading to the loss of fragments with 1 to 6 carbon atoms: in opposition to the terphenyl isomers, the value of $I(-C_6)$ for quaterphenyl isomers containing ortho-bonds is considerably higher than for the others, and the relation $I(-C_2) > I(-C_1)$ for the isomers containing only meta- and para-bonds is not anymore fulfilled. The latter means an interesting change in the characteristic features of the mass spectra of the serie benzene, diphenyl, p-terphenyl, p-p-quaterphenyl.

It would be of interest to gain information on the probabilities for rupture of the C-C-bonds between the rings in ortho-, meta- and para-position. In general, considerations of this type have a high degree of uncertainty as only little is known on the structure of the fragment ions observed and the steps involved in the fragmentation processes. Therefore, essential assumptions become necessary. In the case of the quaterphenyls however, the existence of six isomers offers the possibility to prove the validity of the assumptions at least to a certain extent.

Supposing that the positive ions containing 18 carbon atoms are formed by simple breakage of the C-C-bond between the rings (partly combined with an additional loss of hydrogen atoms) and taking into account that the strength of this bond is only little influenced by the isomeric position of the fourth ring on the other end of the chain, one would expect that certain values of probability could be attributed to the processes of ring loss, which depend only on the isomeric position of the separated ring itself and are independent of the isomeric character of the residual fragment.

As it is justified to assume that the total ionization for the different quaterphenyl isomers is equal (see page 16), the relative group ionization $I(-C_6)/T.I.$ is a measure for the probability of the processes of this type, which lead to the formation of a single charged residual ion.

If W_{xy} describes the probability for loss of the ring in x- or y-position in a x-y-quaterphenyl (measured in terms of its relative group ionization), W_x and W_y the probabilities for loss of the ring in x- or y-position respectively, the general equation

$$W_{xy} = W_x + W_y$$

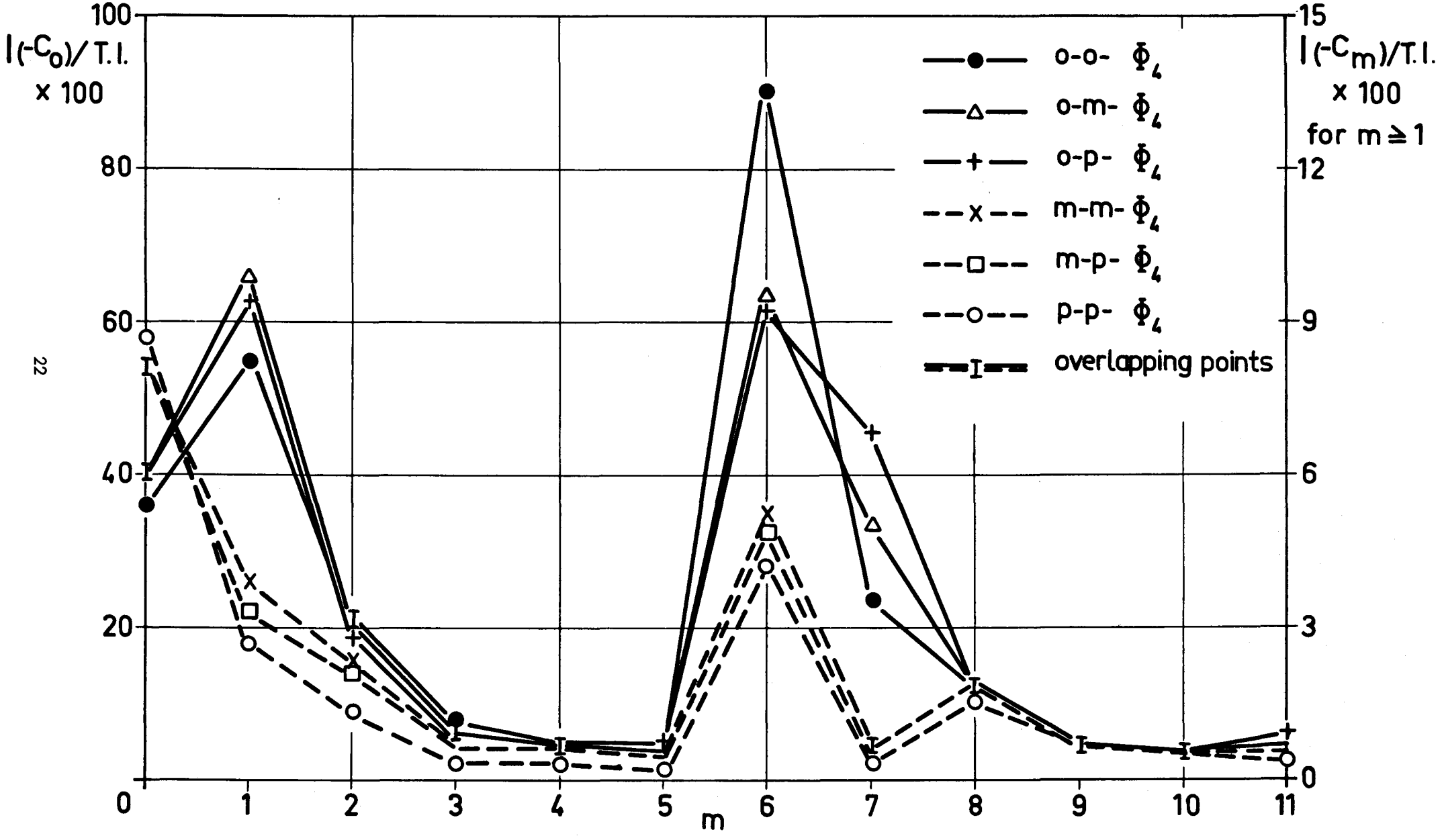
or especially

$$W_{xy} = \tfrac{1}{2} W_{xx} + \tfrac{1}{2} W_{yy}$$

should be valid.

In table 5, the relative group ionizations for the unsymmetrical isomers calculated in this way are compared with the observed values. The agreement is remarkable. As cor-

Fig.2 Relative Group Ionizations $I(-C_m)/T.I.$ for the Quaterphenyls



responding considerations for the group ionizations $I(-C_1)$ to $I(-C_5)$ and $I(-C_7)$ to $I(-C_{11})$ (this means for processes which necessarily include the opening of a ring) show unsystematic deviations up to 50 % between the values observed and those calculated from the symmetrical isomers (*), this result supports the previous assumption that the fragment ions containing 18 carbon atoms are formed by rupture of the C-C-bond between the rings (partly combined with additional loss of hydrogen atoms) and that there are probably no ring-opening processes involved.

TABLE 5
Relative Group Ionizations $I(-C_6)/T.I.$

Compound	$I(-C_6)/T.I. \times 100$ observed	« calculated »	deviation
o-m-Quaterphenyl	9.48	9.37	1.2 %
o-p- Quaterphenyl	9.23	8.89	3.5 %
m-p-Quaterphenyl	4.83	4.70	2.7 %

A ratio of 100 (ortho) : 38 (meta) : 32 (para) would result from the relative group ionizations $I(-C_6)/T.I.$ of the symmetrical isomers for the probabilities of processes of this type on quaterphenyls.

If especially those processes are considered, which lead only to the loss of a C_6H_5-group, corresponding considerations can be based on the ratio of the intensity $I(C_{18}H_{13})$ of ions of the type $C_{18}H_{13}^+$ to the total ionization T.I. as a measure for the probability.

The results (table 6) show also a good agreement and a ratio of 100 (ortho) : 12 (meta) : 7 (para) is found for the ratio of the probabilities of these processes on quaterphenyls.

From comparison of the two probability ratios follows that under bombardment with electrons of 70 eV energy fragmentation processes which lead to the loss of a C_6H_5-group are relatively more frequent combined with dissociation of additional hydrogen atoms from the residual ion if the C_6H_5-group is in meta- or para-position than if it is in ortho-position.

TABLE 6
The Relative Intensities for $C_{18}H_{13}^+$-ions

Compound	$I(C_{18}H_{13})/T.I. \times 100$ observed	« calculated »	deviation
o-m-Quaterphenyl	2.36	2.25	4.6 %
o-p- Quaterphenyl	2.16	2.15	0.5 %
m-p-Quaterphenyl	0.381	0.376	1.3 %

(*) Also for hydrogen loss processes, no agreement can be found between the probabilities for C-H-bond rupture (characterized by the ratio $I(P\text{-}1)/T.I.$ or $\sum_{n=1}^{8} I(P\text{-}n)/T.I.$ see table 4) observed on the unsymmetrical isomers and those calculated from the symmetrical ones.

5.5. Survey on the Fragments lost most frequently

With regard to the possible connection between the fragments formed by electron bombardment in the mass spectrometer and the light products obtained by radiolysis of polyphenyls, the mass numbers of the most frequently lost light fragments and their atomic compositions have been compiled in table 7.

The relative intensities, corrected for isotopic contributions, are given in percent of the total ionization. Fragments for which these values are below 1 % have been omitted, also those with a mass higher than one half of the molecular weight because of the uncertainty in the intensity values due to double charged contributions to the complementary ions. The relatively small corrections (in general below 5 % of the value) which would result from processes in which the complementary ion is double charged have not been applied. If the intensity of the positive ion corresponding to the lost fragment is not negligible, the value has been marked by « + ». This is especially the case in the C_3H_3-formation from diphenyl.

Comparison of these data with the compcsition of the light products formed in radiolysis is difficult for two reasons:

a) Electronbombardment in the mass spectrometer takes place in the gaseous phase, whereas all irradiation experiments have been performed in the liquid phase.
b) Until now, there exists only little information on comparative irradiation experiments performed on the different pure isomers, especially the radiolysis products of quaterphenyls are not known.

In the following the most essential predictions from the mass spectrometric data are confronted with some of the results of radiolysis experiments:

Hydrogen: Due to the data given in table 7, hydrogen is expected as the main radiolysis product of diphenyl and all terphenyls and also as one of the main compounds obtained in the radiolysis of quaterphenyls containing ortho-bonds.

All authors (12 - 14) agree that hydrogen is the main gaseous product formed at least in the initial stage of the radiolysis of diphenyl and all terphenyls at temperatures below 350 °C.

Methane: According to mass spectrometry, methane should be obtained preferably in the radiolysis of the ortho-isomers of the ter- and quaterphenyls and in smaller quantities from diphenyl.

Bates et al. (14) found the quantity of methane formed from ortho-terphenyl in electron or pile irradiation studies at 350 °C to be about twice as high as from meta-terphenyl. This is measured for a dose up to about 30 watt · hr · g^{-1} in electron irradiation and up to about 6 watt · hr · g^{-1} in pile irradiation experiments.

From diphenyl, Hall and Elder (13) observed no methane in ^{60}Co irradiation experiments at 74 to 82 °C and with a maximum dose of about 0.2 watt · hr · g^{-1}. Rayroux and Baertschi (15) found about 6 % methane in the gases formed by in-pile irradiation at 35 to 40 °C, however at a dose which was about 100 times higher than in the experiments of Hall and Elder.

Bates et al. (14) report at the same dose but at a temperature of 300 °C also about 5 % methane in the total gas produced.

C_2-Hydrocarbons: The mass spectrometric data would predict the formation of acetylene from diphenyl, ethylene from the terphenyls and ethane mainly from the ortho-quaterphenyls as the major C_2-hydrocarbons.

Bates et al. (14) found in agreement with the work of Hall and Elder (13) acetylene as the main hydrocarbon in ^{60}Co-, electron- and pile irradiations of diphenyl for a dose up to 4.8 watt.hr.g^{-1} and a temperature below 250 °C. At higher temperatures, Bates et al. (14) observed a tendency towards saturation of the C_2 species resulting in the preferable formation of ethylene and ethane due to consecutive hydrogenation.

TABLE 7

Survey of the Fragments lost most frequently

Mass number of lost fragments	Atomic composition		Relative intensities									
			Φ_2	o-Φ_3	m-Φ_3	p-Φ_3	o-o-Φ_4	o-m-Φ_4	o-p-Φ_4	m-m-Φ_4	m-p-Φ_4	p-p-Φ_4
1		1 H	12.2	12.7	5.13	2.26	4.35	5.03	4.25			
2		2 H	9.59	7.47	6.04	5.20	1.35	1.79	2.01	1.07	1.08	1.00
3		3 H	2.90	2.18	2.04	1.77	1.43	1.72	1.62	1.07	1.01	
4		4 H		3.76	2.90	2.50	2.11	2.61	2.64	1.56	1.49	1.34
15	1 C	3 H		7.19	1.74	1.19	2.21	3.10	2.66			
16	1 C	4 H					1.46	1.57	1.50			
17	1 C	5 H					4.24	4.86	4.86	2.57	2.23	1.96
26	2 C	2 H	1.24									
28	2 C	4 H		2.74	2.19	2.13						
30	2 C	6 H					1.47	1.46	1.36			
39	3 C	3 H	1.60+									
77	6 C	5 H					4.88+	2.86+	2.60+			
78	6 C	6 H			1.89	2.00	4.82	3.24	3.15	1.65	1.55	1.45
79	6 C	7 H			1.03	1.12	1.01	1.07				
80	6 C	8 H					2.39	2.15	2.22	1.71	1.61	1.51
91	7 C	7 H					3.56+	4.91+	6.62+			
104	8 C	8 H					1.20	1.07	1.06			

Rayroux and Baertschi (15), who worked at low temperature (35 to 40 °C) but with the larger dose of about 20 watt · hr · g^{-1}found ethylene as the major C_2-hydrocarbon.

Concerning the C_2-radiolysis products from terphenyls, Bates et al. (14) come to the conclusion that a low dose at 350 °C on the meta- and para-terphenyl seems to produce more ethylene and ethane and less acetylene than arises from diphenyl.

However only in some electron irradiation experiments these authors observed a higher quantity of ethylene than ethane. Especially in pile irradiations, the amount of ethane formed was considerably larger.

Low Boilers: The relative high amount of fragments containing 6 carbon atoms in the mass spectra of the ortho-quaterphenyls would suggest that the low boiler fraction of the radiolysis products is the largest for these compounds. Compared to this, it should be much smaller for the terphenyls, and especially for the ortho-isomer.

Unfortunately there exist to our knowledge no published data on irradiation experiments which allow a prove on this prediction.

From these considerations it seems that some agreement between the fragments obtained in the mass spectrometer and the light radiolysis products is found if a small total dose is integrated at low temperature. Mass spectrometric data may therefore gain some importance in the determination of the primary products formed in the first stage of the radiolytic decomposition. In the case of the C_2-hydrocarbon formation from terphenyls it seems that the fragments obtained in a mass spectrometer correspond better with the radiolysis products from electron irradiations than with those from pile irradiation experiments.

6. CONCLUSION

A comparison of the mass spectra of diphenyl and the ter- and quaterphenyls shows a considerable different behaviour of all compounds containing ortho-bonds with respect to the others. The results indicate that this is probably caused by a principally different fragmentation process for ortho-isomers because of the higher interaction between the rings in this position. A better understanding of the mechanism may be expected from studies mainly on ^{13}C-labeled ortho-terphenyl and diphenyl or p-terphenyl.

From the analytical point of view this different behaviour means that satisfactory precision can be expected from the 70 eV spectra as far as there is no need to distinguish between meta- and para-isomers.

From the total of the data obtained it can be concluded that ortho-isomers are the least, para-isomers the most stable of these compounds against electron bombardment of 70 eV energy.

Some agreement is found between the fragments obtained in the mass spectrometer and the light radiolysis products observed in irradiation experiments if a small total dose is integrated at low temperature.

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