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EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM

**PHENYLATION OF BIPHENYL, o- AND m-TERPHENYL  
AND THEIR MIXTURES WITH BENZOYLPEROXIDE.  
DETERMINATION OF RELATIVE REACTIVITIES AND  
PARTIAL RATE FACTORS**

by

H. STANGL and G. JUPPE

1969



Joint Nuclear Research Center  
Ispra Establishment — Italy

Chemistry Department

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## ABSTRACT

The phenylation of biphenyl, o- and m-terphenyl with benzoylperoxide as phenyl radical generator is investigated. All expected terphenyl- resp. quaterphenyl-isomers are formed and are determined by gas chromatography. In addition to well-known products from benzoylperoxide decomposition, small amounts of benzene are found qualitatively in all experiments, and traces of biphenyl in the case of terphenyl solvent. Relative reactivities for the phenylation are determined from competition experiments with the three polyphenyl solvents, using a new method in evaluating the experimental results. The earlier procedure is critically discussed and compared. Rate constants relative to biphenyl are  $1.40 \pm 0.08$  for o-terphenyl and  $1.66 \pm 0.1$  for m-terphenyl. The value of 1.18 for m-terphenyl reactivity relative to o-terphenyl, calculated from the above results, is also evaluated experimentally from a competition experiment. Partial rate factors for the different molecule positions are determined from isomer ratios and the influence of resonance stabilization and steric hindrance is discussed. Numerical increments for these contributions, deduced by this analysis, allow a rough calculation of the probable reactivity of p-terphenyl against phenyl radicals (2.3 compared to biphenyl). A first estimation is made on this basis also for quaterphenyl and triphenyl-benzene reactivities.

## KEYWORDS

CHEMICAL REACTIONS  
BIPHENYL  
TERPHENYL-ORTHO  
TERPHENYLS  
BENZOYLPEROXIDES  
REACTION KINETICS

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In an ORGEL type reactor the organic coolant will be exposed to the simultaneous decomposing action of both irradiation and heat. The degradation of the organics due to pyrolysis will be exceeding the radiolytic decomposition at elevated temperatures. A detailed knowledge of the individual steps of the degradation processes and their sequences is of primary importance for a thorough understanding of the over-all decomposition under in-pile conditions.

As primary process for the pyrolytic decomposition of bi- and terphenyl molecules a formation of phenyl, biphenyl, and terphenyl-radicals and hydrogen atoms is currently discussed<sup>1)</sup>. Further attack of these highly reactive species would lead to the production of phenylated and hydrogenated intermediates or end products.

Each individual component in a mixed polyphenyl coolant is expected to compete with the others in its reaction with the primarily formed hydrogen atoms, phenyl and polyphenyl radicals. If their reactivities are different, this should consequently result in differences in the rates of decrease between biphenyl, o-, m-, and p-terphenyl and lead to a continuously changing composition of the coolant mixture. It should become especially obvious after long pyrolysis times, after repeated bulk separation and reuse of the bi-phenyl-terphenyl fraction after the purification process. If for example p-terphenyl exhibits the smallest reactivity towards the above radical species an enrichment of this compound in the cooling mixture would consequently appear. This would be highly undesirable for reactor operation, due to the high melting point of p-terphenyl and to its tendency to crystallize at higher percentages.

For this reason we studied the phenylation of biphenyl, o-, and m-terphenyl and of mixtures of these compounds. Phenyl radicals were produced by the thermal decomposition of benzoyl peroxide and the experiments performed at 100°C.



1. INTRODUCTION (\*)

Phenylations with benzoyl peroxide as phenyl radical generator have been very widely and intensively investigated<sup>2)</sup>. Of the work dealing with the mechanism of the reactions one can find two distinct areas of research:

1) The kinetics of the thermal decomposition of benzoyl peroxide in aliphatic and aromatic solvents.

2) Investigation of the products formed in the benzoyl peroxide decomposition in mainly aromatic solvents and the evaluation of a reactivity scale of these aromatics.

All research dealing with the second point is based on the fundamental works of Hey and coworkers who since 1934<sup>3)</sup> have continuously been active in this field. They and a few other groups investigated a whole range of substituted benzenes, and some simple aromatics, and derived reactivities from competition experiments and so called "partial rate factors" from isomer distribution. The limiting factor in covering also other aromatic substances was the analytical difficulty of product separation and isomer determination, especially with chemically similar systems. This was most probably the reason why only biphenyl was investigated out of the polyphenyls so far<sup>4), 5), 6)</sup> and even then the relative reactivity as compared to benzene had to be found by an indirect method<sup>4)</sup>. Later, with the improvement of analytical methods, a correction of the value was necessary<sup>7)</sup>. Recent developments of gas chromatography allow now quite exact analysis of higher polyphenyls, mainly the quaterphenyls, and the experiences won in our laboratories in the analysis of organic reactor coolant<sup>8)</sup> enabled us to attack the problem of phenylation of terphenyls and mixtures of biphenyl with terphenyls for the evaluation of reactivities and partial rate factors.

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(\*) Manuscript received on 2 February 1969.

## 2. EXPERIMENTAL PART

### 2.1. MATERIALS

Benzoyl peroxide was a Fluka reagent "purissimum" grade. Its peroxide content was found by titration with sodium thiosulfate solution: In a round flask with condenser were placed 0.2 g. peroxide, 30 ml. acetic acid, 10 ml. petrol ether and about 2 g. potassium iodide. The mixture was heated for 20 minutes under reflux, then the content diluted with 50 ml. distilled water and titrated with 0.1 n thiosulfate solution. 1 ml. 0.1 n sodium thiosulfate resembled 12.11 mg. benzoyl peroxide. The Fluka reagent was found to be 99.2% pure.

Biphenyl (British Drug House Laboratory reagent) contained three unidentified lower boiling impurities of about 0.1% as shown by gas chromatography. The water content as analyzed by Karl Fischer method was 92 p.p.m. Flushing over night with nitrogen at 100°C lowered it to 48 p.p.m.

o-Terphenyl (Merck) was recrystallized three times from methanol and found free of isomers by vapor phase chromatography. The water content was initially 390 p.p.m., after nitrogen treatment 95 p.p.m.

m-Terphenyl (Merck) was fractionally distilled and was also found isomerically pure. It contained 52 p.p.m. of H<sub>2</sub>O.

"PP" (purissimo) nitrogen was further purified by sweeping it over a tower with BTS catalyst (Badische Anilin- & Soda-Fabrik) at 80°C and then through a tower with molecular sieve (Union Carbide type 4A, site 1/8 PLTS). This treatment removes oxygen and water.

## 2.2. METHOD AND APPARATUS

Benzoyl peroxide was decomposed at  $100^{\circ} \pm 0.2^{\circ}$  in 0.2 molar solutions, using 0.01 moles and 50 g of solvent or solvent mixture<sup>\*)</sup>. The apparatus for decomposition and carbon dioxide measurement consisted of a three necked flask with ground joints, set into a thermostat and fitted with reflux condenser and gas inlet for nitrogen, reaching to the bottom of the flask. The top of the reflux condenser (Dimroth type) was connected to a cooling trap, kept at  $-60$  to  $-70^{\circ}$  by means of acetone-dry ice mixture to condense water and organic traces. The exit of the trap led to a U-shaped absorption-tube which was filled with carbon dioxide adsorbing reagent (ascarite) mixed with calcium chloride<sup>\*\*)</sup>. This tube was carefully weighed before and after the decomposition. Its exit was covered by a small tube filled with calcium chloride to prevent back diffusion of water vapor.

Before the reaction, all solvents or solvent mixtures were flushed at  $100^{\circ}$  over night with a slow stream of dry and oxygen free nitrogen to remove water and air. This method for removing the water was as effective as a repeated degassing procedure under vacuum.

The benzoyl peroxide was dissolved at  $80$  to  $90^{\circ}$  by vigorous shaking and the reaction flask quickly inserted again into the thermostat. A slow stream of dry and oxygen free nitrogen was used then during the decomposition to sweep all carbon dioxide into the absorption tube. After about 16 hours (over night run) all carbon dioxide had been collected.

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\*) The density of polyphenyl is approximately 1 at the melting point.

\*\*) It turned out necessary to mix the ascarite with other corned reagent, e.g. calcium chloride to avoid clogging.

### 2.3. WORKING UP PROCEDURE

After completion of the decomposition, the solutions were diluted with 50 ml of pure benzene and extracted four times with 10% ice cold sodium carbonate solution; the aqueous extract (around 80 ml) was washed with a little benzene which was added to the organic part. The sodium carbonate extract was acidified with half concentrated sulphuric acid and the solution extracted three times with a total of 75 ml of ether. The ether solution was dried with calcium chloride, the ether evaporated and the residue weighed. This residue was not pure benzoic acid (m.p. 101-108°) but contained also higher acids\*).

The benzene solution was also dried with calcium chloride, filtered, and then filled up to 100 ml or 200 ml in a volumetric flask for the gas chromatographic determination.

### 2.4. GAS CHROMATOGRAPHIC ANALYSIS

Analytic determination of the phenylation products was performed by gas chromatography (Packard Gas Chromatograph, model 7508). We used the solutions without removal of the high amount of solvent polyphenyl. Distillation in vacuum of even only a part of the polyphenyl changed the composition of the residue considerably. It was checked by test runs that a large amount of biphenyl or terphenyl in the solution did not influence the analytical value for a higher polyphenyl as compared to its solution in pure benzene.

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\*) see Table I.

A 2.5 m., 1/4 inch diameter, steel column, filled with 10% silicone grease and 0.2% bentone on celite (60-80 mesh), was used at a temperature of 250°C and a nitrogen gas flow of 60 cc./min. Detector and inlet temperature were 290°C. The flame ionization detector (Packard Gas Chromatograph) was fed with 30 cc./min. hydrogen and 200 cc./min. air.

This column did not allow the separation of o,o-quaterphenyl and 1,2,3-triphenyl-benzene, and o,p-quaterphenyl and 1,2,4-triphenyl-benzene. The former pair is only separable on inorganic columns (LiCl, CsCl), for the latter seems to exist no reproducible method so far.

Evaluation of the peaks was made by planimetric method (half width and height) with calibration mixtures. Because this method is normally not too accurate and some peaks, especially of some higher polyphenyls were asymmetric, the calibration mixtures were chosen very close to the actual values and each sample chromatogram enclosed by chromatograms of the appropriate calibration mixtures. In this way the analysis became very accurate and the average error was well below  $\pm$  3%. The calibration curves were strictly linear. As each experiment was done in duplicate and for each analysis were used at least two injections four values could be compared. The deviation between the two runs of an experiment was even smaller than the error from gas chromatography.

### 3. RESULTS

#### 3.1. THE PROBLEM OF THE CORRECT DETERMINATION OF RELATIVE RATE CONSTANTS

Reactivities or relative rate constants are determined by competition experiments where an insufficient amount of reactant can choose between several possible reaction partners, which are present in large excess. For easier analyses one chooses normally only a two component competition experiment and furthermore prefers an equimolar ratio of the partners, if the reactivities are not too different. Hey and coworkers calculated the relative rate constants of aromatic solvents simply by dividing the analytically determined yields (in mole-equivalents) of the two phenylation products, i.e. total molar yield of the phenylation product from one compound divided by the total yield of the second phenylation product.

This may be done if the following conditions are met:

- 1) phenylation of the two competing compounds to the corresponding aromatic products is the only possible reaction of the phenyl radical and no byproducts are formed,
- and 2) the analytic determination of the two products accounts for practically 100% of the original phenyl radical amount,
- or 3) for the special case that, though condition 1) is not fulfilled, the amount of side and consecutive reactions is the same for both competitive phenylations. This could be the case if these side product formations are solvent independent.

Doubts had already been expressed some time ago<sup>9), 10), 11), 12), 13)</sup> as to the validity of such determined rate constants and partial rate factors, but evidence was presented that at least for some cases and for certain changes of the reaction conditions the original determination held well<sup>14), 15), 16)</sup>.

As condition 1) is hardly ever fulfilled, Hey tried in part of his work<sup>17)</sup> to correct for side reactions by accurate analyses of the higher molecular products. Competitive experiments which include nitrobenzene are said to give practically no higher boiling material<sup>7),18)</sup>, though with the other compound alone phenylation may proceed with appreciable formation of high molecular side products<sup>9),10),12)</sup>. This means that only when neglecting lower boiling byproducts, condition 1) would be valid in such cases. Morrison and coworkers<sup>14)</sup> carried out benzoyl peroxide decompositions in the presence of excess oxygen. They found no change of the partial rate factors and relative rate constants though the absolute yields of phenylated solvents were quite augmented. They concluded that main and side reactions in the competitive phenylations must have been influenced to the same extent and that therefore no change was detectable. Nevertheless the absolute values of the reactivities could still be wrong. Furthermore, any concentration dependence of the phenylation product yields, if different for the two competing solvents, would also make the evaluated reactivity concentration dependent and not generally valid.

It is very important to control also condition 2) very carefully, that is the complete analytical recovery of all phenyl radical derived products, because even small losses influence the value of the relative rate constant quite appreciably<sup>\*)</sup>. For that control one must know the amount of carbon dioxide which was formed in the decomposition, because it resembles practically the amount of available phenyl radical (see later). The measurement of carbon dioxide in competitive experiments was never mentioned in Hey's work. They added up all other products, including benzoic acid

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\*) compare Lit. 3 with 6.

and residue to compare it with the original amount of benzoyl peroxide and reached in most cases only around 85%, even in experiments with nitrobenzene<sup>17)</sup>. As benzoic acid can be accurately determined, the uncertainty of where have gone the 15% concerns mainly the especially interesting phenyl radical derived products, and this would in turn lead to calculated reactivities which bear eventually an appreciable error.

### 3.2. THE NEW APPROACH TOWARDS REACTIVITY DETERMINATION AND EXPERIMENTAL RESULTS

A possibility to avoid the uncertainty, introduced by the occurrence of side reactions in the competition experiment is the comparison with the phenylations in each of the two pure solvents alone. From there, one gets the distribution of phenyl radicals into phenylated solvent and into any kind of side product in both cases, provided one knows the over-all phenyl radical production. The latter may be directly taken from the yield of carbon dioxide, as will be discussed later.

From decompositions of benzoyl peroxide in benzene, biphenyl, o- and m-terphenyl and its mixtures at different temperatures it became obvious that the amount of carbon dioxide was solvent dependent even in those similar systems. From table I follows that benzene differs markedly by the high amount of carbon dioxide produced, as compared to the polyphenyls and that this behaviour is also pronounced in its mixtures.



TABLE I

Yields of  $\text{CO}_2$  respectively  $\text{C}_6\text{H}_5$  and benzoic acid from 0.01 mole benzoyl-peroxide at different temperatures

Solvent		Temp.	$\text{CO}_2, \text{C}_6\text{H}_5$ moles $\cdot 10^3$	benzoic acid <sup>*)</sup> moles $\cdot 10^3$	total %
Benzene		80°	13.4	3.8	86
Biphenyl		80°	10.0	7.4	87
o-Terphenyl		80°	10.0	7.4	87
m-Terphenyl		90°	9.6	7.8	87
Benzene/ $\phi_2$	1:1	80°	11.6	5.7	86.5
Benzene/o- $\phi_3$	1:1	80°	11.8	5.9	88.5
Benzene/m- $\phi_3$	1:1	80°	11.0	6.5	87.5
Biphenyl		100°	10.4	6.8	86
o-Terphenyl		100°	10.2	6.9	85.5
m-Terphenyl		100°	9.8	7.3	85.5
$\phi_2$ /o-Terphenyl	1:1	100°	10.3	6.6	84.5
$\phi_2$ /m-Terphenyl	1:1	100°	10.0	7.4	87
o- $\phi_3$ /m- $\phi_3$	1:1	100°	9.9	7.2	85.5
Biphenyl		130°	12.4	5.4 <sup>**)</sup>	89
o-Terphenyl		130°	11.2	6.0	86
m-Terphenyl		130°	10.6	6.7	86.5

\*) As directly extracted. Contains from 2 to 5% higher acids.

\*\*\*) Contains 8% higher acids, not considered in the calculation.

It would probably complicate the correct interpretation of competition experiments in the above mentioned way if the carbon dioxide resp. phenyl radical yield differs appreciably when passing from the pure solvent to the mixture. Therefore, we dropped for the moment the idea of a reevaluation of the benzene-biphenyl reactivity. Changing carbon dioxide yields would most probably effect also the main product to byproduct ratio and our procedure assumes that this ratio stays the same for each partner, in the pure solvent and in the competition mixture. Thus, we chose for our experiments only biphenyl, o- and m-terphenyl and their mixtures, because at 80° and 100° they give practically the same carbon dioxide resp. phenyl radical yields and, as will be shown later, it was proved by the results that also the above assumption is valid for these cases. At 130° where exact temperature control and carbon dioxide measurement become already very difficult\*) the values differ quite appreciably. These higher temperature runs have not been further investigated, but one might foresee a different product composition.

We worked in our experiments at a constant temperature of 100°, which was well above all melting points ( $\phi_2$  70°; o- $\phi_3$  57°; m- $\phi_3$  86°) and with a concentration of 0.2 mole/l. Due to its high melting point (213°) and its low solubility, experiments with p-terphenyl could not be included in this work.

Table II shows the results of phenylations in pure solvents and in three equimolar mixtures. Product yields are given in moles from 0.01 mole of benzoyl peroxide decomposed. The sum of benzoic acid and carbon dioxide is throughout rather constant, from 0.0169 to 0.0175 mole.

\*) N.H.Ray<sup>19)</sup> has determined the half-life of benzoyl peroxide:

Temp.	$k_1$ ( $10^{-2}\text{sec}^{-1}$ )	Half-life (sec)
143°	4.6	15
150.5°	8.2	8.5
166°	45	1.5

TABLE II

Product yields from decomposition of 0.01 mole  
benzoyl-peroxide in 50 cc polyphenyl solvent at 100°C

Experiment		CO <sub>2</sub> (resp. C <sub>6</sub> H <sub>5</sub> <sup>•</sup> ) (mole · 10 <sup>3</sup> )	Benzoic acid (mole · 10 <sup>3</sup> )	CO <sub>2</sub> + benzoic acid (mole · 10 <sup>3</sup> )	Phenylated Derivative of		% Yield rel. to C <sub>6</sub> H <sub>5</sub> <sup>•</sup>
Solvent 1 (1:1 molar)	Solvent 2				Solvent 1 (mole · 10 <sup>3</sup> )	Solvent 2 (mole · 10 <sup>3</sup> )	
Biphenyl	-	10.3	6.8	17.1	6.91 <sup>d)</sup>	-	67.0
o-Terphenyl	-	10.2	6.9	17.1	7.60	-	74.5
m-Terphenyl	-	9.8	7.3	17.1	8.16	-	83.2
o-Terphenyl	Biphenyl	10.3	6.6	16.9	4.37	2.81 <sup>a)</sup>	69.7
m-Terphenyl	Biphenyl	10.1	7.4	17.5	5.02	2.44 <sup>b)</sup>	73.9
m-Terphenyl	o-Terphenyl	9.9	7.2	17.1	4.46 <sup>c)</sup>	3.41 <sup>c)</sup>	79.5

a) Calculated from m- and p-terphenyl values alone

b) " " o-terphenyl alone

c) " " percentage of 1,3,5-triphenyl benzene, m,m-quaterphenyl and  
m,p-quaterphenyl

d) Karelsky and Pausacker<sup>6)</sup> found 0.64 mol per mol benzoyl-peroxide

Karelsky and Pausacker<sup>6)</sup> reported for the phenylation of biphenyl, though carried out at a higher concentration, the same result, 1.71 mole per mole benzoyl peroxide for the sum of carbon dioxide and "1st acid", i.e. the directly extracted acid. For the "2nd acid", the acid from ester saponification, they found 0.24 mole per mole benzoyl peroxide. We did not determine the ester content in our reaction mixtures. In an orientating saponification of a o-terphenyl run we found only 0.0014 mole of benzoic acid and around 0.0007 mole of solvent phenol. A peak corresponding probably to benzoic acid-phenylester disappeared after the treatment.

Column 5 gives the yields of terphenyls and/or quaterphenyls as analyzed by gas chromatography, column 6 the percentage yield of these products based on the amount of carbon dioxide resp. phenyl radical of column 3. These yields rise from biphenyl to o-terphenyl to m-terphenyl and are somehow in between in the mixtures. The missing part of the phenyl radicals has reacted to byproducts: 33% in biphenyl, 25.5% in o-terphenyl, and only 16.8% in m-terphenyl. As can be seen from table II and will be shown in detail below, m-terphenyl is also the most reactive of the three.

In preliminary experiments we determined qualitatively for all the reaction solutions of table II after the decomposition a little amount of benzene as byproduct, carried away by the nitrogen stream, and traces of biphenyl in the reaction solutions from terphenyls.

No attempt was made towards a quantitative analysis of benzene<sup>\*)</sup> and biphenyl or the determination of other higher molecular phenylation products. Traces of water were swept out of the reaction mixtures by the nitrogen stream and found together with the benzene in the dry ice trap.

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\*) Even at 100° benzene will be mainly dissolved in the polyphenyl solvent and only some part escapes into the gas phase.

As indicated in the table, some of the values of total yields had to be calculated from the yield of only one or a few isomers in the competition experiments. In the biphenyl-o-terphenyl run only m- and p-terphenyl could be evaluated from the gas chromatogram, whereas in the biphenyl-m-terphenyl case, it was only the o-isomer, because the relatively small amount of p-terphenyl was hidden under the m-terphenyl solvent peak.

These calculations are based on the isomer distribution in the reaction product from the pure solvents as shown in table III. A comparison of column 3 with 5 and 4 with 6 shows that there is only a small change of that distribution in going from pure solvent to solvent mixture. Values in brackets are totally or partially calculated.

Unfortunately, two isomer pairs could not be separated: o,p-quaterphenyl and 1,2,4-triphenyl benzene, and o,o-quaterphenyl and 1,2,3-triphenyl benzene<sup>\*)</sup>. But as the two quaterphenyls cannot be formed in the phenylation of m-terphenyl, a complete isomer analysis is possible for pure m-terphenyl and biphenyl/m-terphenyl runs. In the o-terphenyl/m-terphenyl mixture three identical quaterphenyl isomers are formed both from o- and from m-terphenyl (1,2,3-triphenyl-benzene, o,m-quaterphenyl, 1,2,4-triphenyl-benzene). Therefore, in this case the overall isomer distribution is completely different from the one in each of the solvents. Three isomers (1,3,5-triphenyl-benzene, m,m- and m,p-quaterphenyl) can only originate from m- and not from o-terphenyl. The sum of the latter three isomers amounts to 33.6% of all quaterphenyls formed when phenylating pure m-terphenyl. The rest of 66.4% can therefore be calculated as absolute amount for the competition experiment leading to the total of all quaterphenyls originating from m-terphenyl. The difference to the experimentally obtained yield represents then the quaterphenyls from the o-terphenyl phenylation in this o-terphenyl/m-terphenyl mixture.

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\*) see experimental part.

TABLE III Isomer distribution in phenylation products (%)

Isomer	S o l v e n t s					
	$\phi_2$	$o-\phi_3$	$m-\phi_3$	$\phi_2/o-\phi_3$	$\phi_2/m-\phi_3$	$o-\phi_3/m-\phi_3$
$o-\phi_3$	44.8			(44.8) <sup>a)</sup>	(44.8)	
$m-\phi_3$	23			(23.2) <sup>b)</sup>	(23)	
$p-\phi_3$	32.2			32.8	(32.2)	
1,2,3-TPB + $o,o\phi_4$		30.9	11.9	29.8	12.7	20.0
$o,m-\phi_4$		22.1	24.7	22.3	25.2	23.0
1,2,4-TPB + $o,p\phi_4$		47	29.8	47.9	31.0	38.1
1,3,5-TPB			4.0		3.3	2.5
$m,m-\phi_4$			11.2		11.7	6.6
$m,p-\phi_4$			18.4		16.1	9.8

a) Calculated values (in brackets)

b) Partially calculated value

TPB = triphenylbenzene

The reactivity or relative rate constant is the relation in which the phenyl radical reacts with one or the other polyphenyl, whereby all products from that phenylation have to be considered if the calculation should not be wrong (see discussion). As only the primary phenylated derivative can be easily determined, the rest may be summed up as unknown compounds from phenylation. For the calculation one must deal with that sum in phenyl radical equivalents, gone to byproducts. It follows that

$$\text{relative rate constant} = \frac{(\text{phenylated solvent} + \text{C}_6\text{H}_5^\bullet \text{ in byproducts})_{\text{solvent 1}}}{(\text{phenylated solvent} + \text{C}_6\text{H}_5^\bullet \text{ in byproducts})_{\text{solvent 2}}}$$

The yields of the two phenylated solvents are known from gas chromatographic analysis (see table II resp. III). Further we know the relation of phenylated solvent to byproduct for each pure solvent and we may assume that it is unchanged for both also in the competition experiment. This allows then, again on the basis of the total phenyl radical production, the calculation of the "phenyl radical, gone to byproduct" part for each solvent in the competition experiment.

These values for the three mixed solvent experiments are shown in table IV, together with the relative reactivities. The value for m-terphenyl versus o-terphenyl reactivity, calculated from the two results above is also given. The experimental error is mainly due to the gas chromatographic analysis. The "sum of all C<sub>6</sub>H<sub>5</sub><sup>•</sup> products" of the table allows the proof for the correctness of the earlier assumption that the relation "phenylated derivative to byproducts" stays for each solvent the same also in the competition experiment. The theoretical value corresponding to the available phenyl radicals (10 · 10<sup>-3</sup> moles) is almost found (see discussion).

TABLE IV

## Relative reactivities

Experiment 1:1 molar		Phenylation of Solvent 1		Phenylation of Solvent 2		Sum of all C <sub>6</sub> H <sub>5</sub> -products mole·10 <sup>3</sup>	Reactivity of <u>Solvent 1</u> Solvent 2
Solvent 1	Solvent 2	Phenylated Solvent mole·10 <sup>3</sup>	C <sub>6</sub> H <sub>5</sub> in byproducts mole·10 <sup>3</sup>	Phenylated Solvent mole·10 <sup>3</sup>	C <sub>6</sub> H <sub>5</sub> in byproducts mole·10 <sup>3</sup>		
o-Terphenyl	Biphenyl	4.37	1.49	2.81	1.38	10.1	1.40 ± 0.08
m-Terphenyl	Biphenyl	5.02	1.01	2.44	1.20	9.7	1.66 ± 0.1
m-Terphenyl	o-Terphenyl	4.46	0.90	3.38	1.16	9.9	1.18 ± 0.04
m-Terphenyl	o-Terphenyl		calculated value				1.18

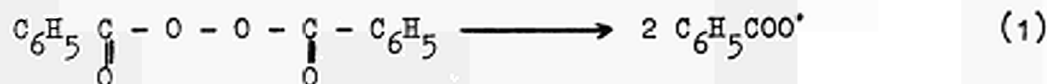


#### 4. DISCUSSION

##### 4.1. GENERAL MECHANISM OF BENZOYL PEROXIDE DECOMPOSITION IN BENZENE

According to a recent reinvestigation of the kinetics of benzoyl peroxide decomposition in benzene by Gill and Williams<sup>20)</sup> the latest version of the reaction mechanism is as follows:

The thermal decomposition in benzene consists kinetically of two reactions: a unimolecular breakdown to give two benzoyloxy-radicals

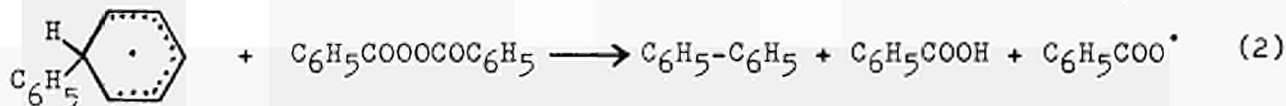


and a radical-induced decomposition of broken order. The first reaction is predominant in dilute solution, the second reaches importance as the concentration is increased. Already Nozaki and Bartlett<sup>21)</sup> found the kinetic equation:

$$-\frac{d(\text{BPO})}{dt} = k_1 [\text{BPO}] + k_2 [\text{BPO}]^{3/2}$$

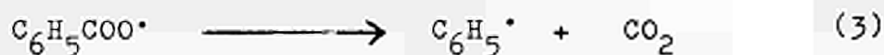
which was evaluated with only slight variation also by the above cited authors.

Term 1 corresponds to the peroxide bond rupture in equation (1), term 2 to the induced reaction, which is in favor of several other possibilities ascribed to the sequence



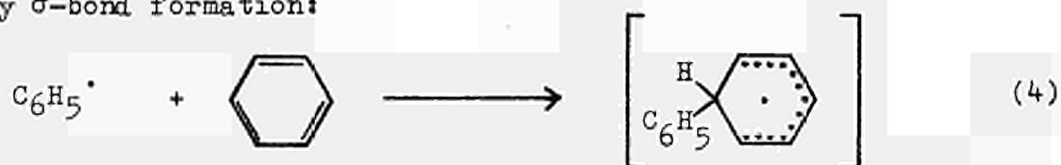
discussed in more detail below.

A part of the benzoyloxy-radicals formed in equation (1) and (2) decarboxylate then spontaneously to give phenyl radicals and an equimolar amount of carbon dioxide:



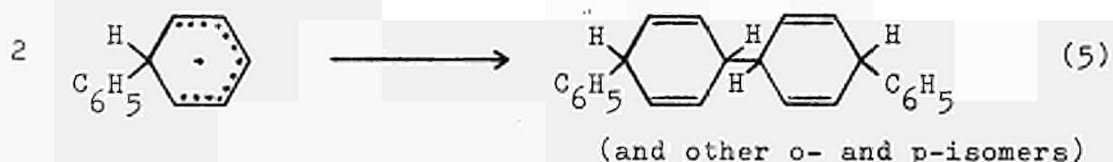
With the formation of the phenyl radical starts the actual phenylation reaction in which we were mainly interested. Unfortunately, the consecutive reactions of the radical are greatly influenced by the presence of undecomposed benzoyl peroxide (equation 2) and benzoyloxy-radicals (see later)\*).

The phenyl radical is highly reactive, though not completely unselective, and attacks immediately the solvent, to which it adds by  $\sigma$ -bond formation:

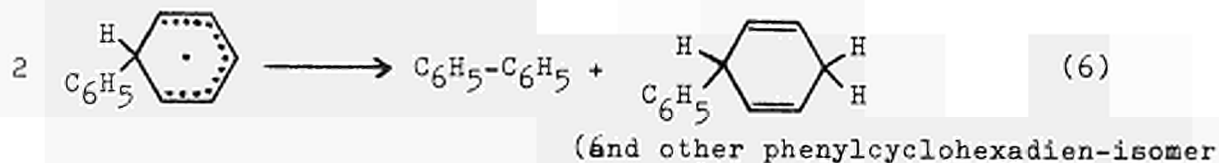


This radical intermediate, a substituted cyclohexadienyl-radical is quite stable through mesomeric effect, compared to the phenyl radical. It cannot add anymore to simple aromatic systems, like benzene or benzoic acid, but is able to wait for further reactions even for another cyclohexadienyl-radical, though its stationary concentration is probably rather low. In addition to equation (2), therefore, two other reactions are important:

the radical dimerization



and the radical disproportionation



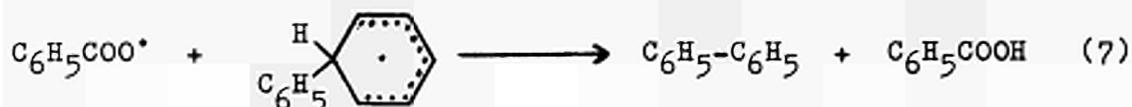
According to equation (6) the phenylation product biphenyl is formed.

\*) There is in fact no ideal phenyl radical generator up till now which would allow a separate investigation of a phenylation without such interference. Of all known phenyl radical generators, benzoyl peroxide seems to be the best in several respects<sup>1)</sup>.

Gill and Williams<sup>20)</sup> found for their kinetic equation an additional term which contributes only to a minor extent to the overall reaction, because  $k_I$  is small

$$-\frac{d(\text{BPO})}{dt} = k_1 [\text{BPO}] + k_I [\text{BPO}] + K_2 [\text{BPO}]^{3/2}$$

They interpreted this term as a first-order induced reaction and ascribed it to the radical combination:



Equation (7) represents the classical reaction by which phenylation with benzoyl peroxide was explained earlier<sup>9),2),7)</sup>. This process is of great importance, not solely because it is the only other way besides (2) by which the phenylation product biphenyl is formed concomitantly with the other main product, benzoic acid, but also because it becomes the principal reaction when one changes from benzene to certain other solvents. This is discussed a little later.

From equations (2) to (7) follow the main products of the benzoyl peroxide decomposition in benzene: carbon dioxide, benzoic acid, biphenyl, different tetra-hydro-quaterphenyls and 1,4- and 1,2-dihydrobiphenyl, the latter two in only small amounts due to their chemical lability. Depending on the concentration, all these compounds amount to 70-90% of the original peroxide groups. Products found in minor quantities are the isomeric terphenyls<sup>2),22)</sup>, phenylbenzoic acids<sup>2)</sup> and compounds containing benzoate groups, especially phenyl benzoate. The former two result from phenyl radical attack on biphenyl and benzoic acid, respectively, i.e. by phenylation of products, or of benzoyl peroxide and are, therefore, characteristic for concentrated solutions. The latter is formed rather concentration independent in part by processes analogous to reactions (4), (2) and (7) with phenyl radical replaced by the benzoyloxy-radical. To some extent phenyl benzoate is also produced in some way directly from benzoyl peroxide, as it is found in decompositions in other solvents. This problem is discussed below.

#### 4.2. MECHANISM IN SUBSTITUTED BENZENES

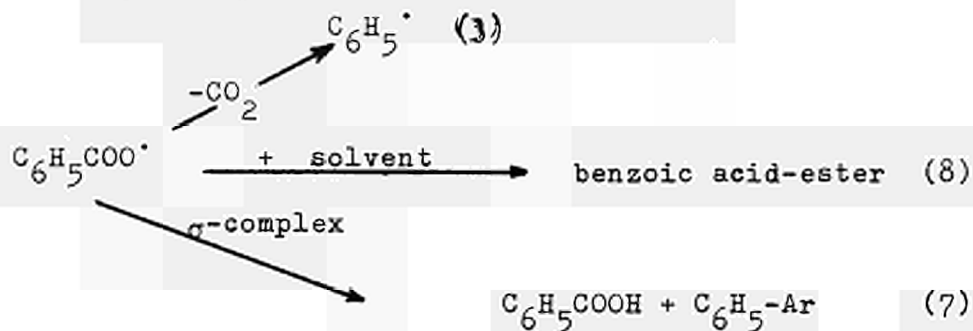
In recent investigations<sup>16), 18)</sup> Gill and Williams showed how the above demonstrated decomposition mechanism for benzene changes in other solvents. In chloro- and bromo<sup>16)</sup> benzene, reaction (2), the 1.5 order induced decomposition, does not occur. Whereas the termination reactions (5) and (6), the dimerization and disproportionation of the cyclohexadienyl radical, are of primary importance for chlorobenzene in dilute solution, the occurrence of reaction (7) is typical for higher concentrations. It is also the only termination reaction in bromobenzene and nitrobenzene<sup>18)</sup> at all concentrations. This means that all cyclohexadienyl radicals are dehydrogenated by benzoyloxy-radicals and dimerization products do not appear. Consequently the benzoic acid yield is not only higher and the carbon dioxide yield lower than in benzene and chlorobenzene but the benzoic acid formation is also equal or higher than the amount of phenylated solvent. This different mechanism in bromobenzene and nitrobenzene is explained by extensive complex formation. For bromobenzene a  $\pi$ -complex between benzoyloxy-radicals and the bromine atom of the solvent is proposed, increasing the stationary concentration for reaction (7). For nitrobenzene a  $\sigma$ -complex between the cyclohexadienyl radical and the nitro group of the solvent is postulated, which inhibits reactions (5) and (6) and enhances again (7) by increased concentration.

Accurate kinetic measurements of the benzoyl peroxide decomposition as for benzene<sup>20)</sup>, chloro- and bromobenzene<sup>16)</sup>, nitrobenzene<sup>18)</sup> and in a less accurate manner for many other solvents<sup>21)</sup> have not been made for biphenyl or the terphenyls. Therefore, nothing is directly known about the reaction mechanism in these solvents. We can only make comparisons of our product compositions with those obtained by the above authors and deduct therefrom some qualitative information.

The benzoyl peroxide decompositions in biphenyl and o- and m-terphenyl yield carbon dioxide and benzoic acid amounts, which are close to those in nitrobenzene<sup>10),18)</sup> and less far away from bromobenzene than from benzene and chlorobenzene values. It may be recalled in this connection that Hey<sup>4)</sup> found the same relative rate constants for the phenylation of nitrobenzene and biphenyl as compared to benzene. Therefore a similar reaction mechanism could be envisaged, though complex formation, due to an electron-negative center, is not possible in polyphenyl solvents. An interesting difference is further that for o- and m-terphenyl the amount of phenylated solvent surmounts the benzoic acid yield, which means that some of the cyclohexadienyl radicals are not dehydrogenated exclusively by benzoyloxy-radicals but possibly still through disproportionation (6). In our opinion all divergence of the reaction mechanism centers around the benzoyloxy-radical and its consecutive reactions:

It can follow three main paths<sup>\*)</sup>:

- 1.) Decarboxylation to phenyl radical and carbon dioxide (equation 3).
- 2.) Direct attack on the solvent to give finally benzoic acid ester (equation 8).
- 3.) Reaction with the  $\sigma$ -complex of reaction (4), according to equation (7), i.e. the H-abstraction to give arylbenzene and benzoic acid..



<sup>\*)</sup> The direct formation of phenylbenzoate, as discussed later, has been neglected.

In the solvents under discussion the benzoyloxylation (8) is always a minor process as the sum of carbon dioxide and the directly extracted benzoic acid is rather high and constant from benzene to m-terphenyl (table I and table V). With very reactive solvents, like naphthalene, this sum is much lower due to a small carbon dioxide yield, and appreciable benzoyloxylation is found then<sup>10)</sup>.

In benzene and chlorobenzene the almost exclusive reaction is the decarboxylation. Both solvents are also quite unreactive for benzoyloxylation. In nitrobenzene and bromobenzene, biphenyl and the terphenyls, the decarboxylation is much less and for the former two cases this is so, because the reaction with the  $\sigma$ -complex is now faster. Suppressed is then also the benzoyloxylation of the solvent, as can be seen from the drop in ester formation from chlorobenzene to bromobenzene (solvent phenols in table V). The reactivity of the nitrobenzene is much higher, and we find, therefore, a small rise in the ester production.

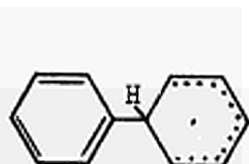
#### 4.3. MECHANISM IN POLYPHENYLS

For biphenyl and the two terphenyls the only alternative to a similar mechanism is an almost complete decomposition according to equation (2), the 1.5 order induced reaction, which results also in simultaneous formation of phenylated solvent and benzoic acid. It should be mentioned again here though, that only for biphenyl these yields are equal, but that in o- and m-terphenyl more phenylated solvent than benzoic acid is found. In the polyphenyl solvents dimerization processes seem to be of minor importance, in contrast to the benzene and chlorobenzene case. This could be explained on the basis that the stationary concentration of the  $\sigma$ -complex is always low and, therefore, induced decomposition would not be favored.

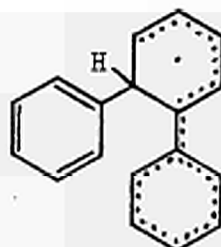
If the dehydrogenation of the cyclohexadienyl- $\sigma$ -complex by benzoyloxy-radical (equation 7) is the preferred reaction if a polyphenyl is solvent, the two possible causes for the change of mechanism resp. the acceleration of this reaction, in comparison to benzene, are:

- 1.) Faster reaction rates of the  $\sigma$ -complexes derived from benzene and biphenyl or terphenyls with the benzoyloxy-radical.
- 2.) Higher stationary concentration of the benzoyloxy-radical in the polyphenyls.

Gill and Williams<sup>16)</sup> argued that the difference in the  $\sigma$ -complexes of chlorobenzene and bromobenzene is not large enough to explain the almost complete shift of reaction mechanism from one to the other solvent and proposed therefore the complex formation for bromobenzene. We have to look for possible differences in the  $\sigma$ -complexes derived from benzene and the polyphenyls. It is difficult to estimate how additional phenyl rings would influence stability and reactivity of these cyclohexadienyl- $\sigma$ -complexes. In the case of the polyphenyls the unpaired electron can be distributed by



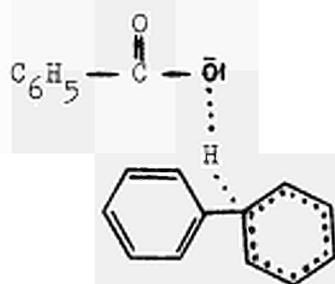
with benzene



with biphenyl (o-substitution)

mesomeric effect also into attached rings, but only with o- and p-addition of the phenyl radical. m-Addition complexes can only be influenced by inductive action, i.e. a slight electron-withdrawing action of the phenyl ring, but this might also lead to some increased stability. Therefore a higher stationary concentration would be possible but the question is still, why the radical dimerization (reaction 5) and the disproportionation (reaction 6)

(equation 7). The H-atom, which must be removed in this process is already in the activated benzylic and allylic position in the benzene derived  $\sigma$ -complex and the additional phenyl groups in biphenyl and terphenyl adducts cannot improve directly its lability. But the activation energy for the hydrogen abstraction is also dependent on the resonance energy gain of the almost aromatic system in the transition state, i.e. shortly before the final loss of the hydrogen atom from the complex. Or with other words, a higher resonance energy gain for the aromatic ring, which releases the H-atom, facilitates



transition state

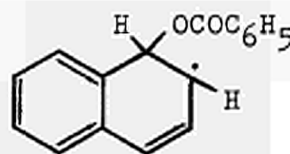
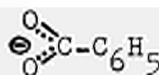
the reaction resp. lowers the activation energy. The difference in resonance energy between the  $\sigma$ -complex radical and the aromatic system for biphenyl and terphenyl or quaterphenyl/triphenylbenzene should be large enough to allow this suggestion.

Another explanation is a higher stationary concentration of the benzoyloxy-radical. Higher peroxide concentration in benzene acutally rises the benzoic acid yield and lowers the carbon dioxide amount<sup>9)</sup>. To explain the difference of mechanism with the same peroxide concentration in benzene and biphenyl/terphenyl one must also propose complex formation with the solvent. As no negative center like in bromobenzene is available, the aromatic system itself must act as electron donor.

Gill and Williams<sup>16)</sup> considered the complex formation with the aromatic nuclei as "less likely", since it would be difficult on this basis to account for the marked difference in behavior between bromobenzene on the one hand, and benzene and chlorobenzene on the other. Now this concept seems to be unavoidable. Complexes



of benzene, biphenyl and the terphenyls with tetracyano-ethylene are known in solution<sup>23)</sup>. They are colored from yellow to violet and, as expected, benzene is weakest in complex formation. These complexes might be of the  $\pi$ - or charge transfer type. One could envisage a continuous rise of interaction of the benzoyloxy-radical with the solvent, from no interaction in benzene, through reversible  $\pi$ -bonding in polyphenyls to partial  $\sigma$ -bonding in naphthalene or other condensed aromatics. This complexing action of the solvent would in turn explain the benzoic acid ester formation as such and the increasing incidence of this reaction in the same sequence (through increasing partial  $\sigma$ -bond character of the complexes).



no interaction  
no esterformation

$\pi$ - or charge-  
transfer complex  
little ester

$\sigma$ -complex  
high ester  
formation

As Gill and Williams<sup>16)</sup> already noted, a charge transfer complex would not only stabilize the benzoyloxy-radical by partial benzoate-anion formation and therefore by a lower probability of decarboxylation, but in turn result in a reduced concentration of the  $\sigma$ -complexes, because less phenyl radicals are formed. This would suppress the dimerization and disproportionation reactions further. Therefore even small differences in the complexing action of the solvent may change the mechanisms to the observed extent.

It has long been known, that a temperature rise favors the decarboxylation in the benzoyl peroxide decompositions, f.i. in benzene. This is noted also with the polyphenyls, especially with biphenyl and only to a minor extent with m-terphenyl, but only at our highest reaction temperature. As at the same time the benzoic acid yield drops, one can assume that the mechanism then changes partly to what it is at 80° for benzene. A reasonable explanation is that the complex formation between the benzoyloxy-radical and the solvent is less intensive at higher temperatures, and this together or without a positive temperature dependence of the decarboxylation itself at the same time<sup>\*)</sup>, The complex with m-terphenyl is stronger than the one with biphenyl and consequently the temperature effect is smaller.

#### 4.4. MATERIAL BALANCE

##### 4.4.1. FATE OF BENZOYLOXY-GROUPS

It is interesting to note that the sum of carbon dioxide and directly extractable benzoic acid accounts rather solvent- and temperature independent for around 87% of all benzoyloxy-groups of the benzoyl peroxide (see tables I, II and V), no matter how different the single values are. Such diverse compounds as benzene, nitrobenzene and methoxy-benzene follow this rule. In some cases, as with benzene and biphenyl<sup>6)</sup> the missing benzoyloxy has been found on saponification of the reaction mixture and the resulting benzoic acid is normally called "ester" or "second" acid, and supposed to appear on estercleavage of benzcarboxylated solvent. It would be surprising that the ester formation in all solvents of table V should be about the same, caused by the missing 13% of benzoyloxy

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\*) A positive temperature dependence of the decarboxylation is the only explanation for the observed effect, if the difference in the reactivities of the  $\sigma$ -complexes is responsible for the change in mechanism.

TABLE V

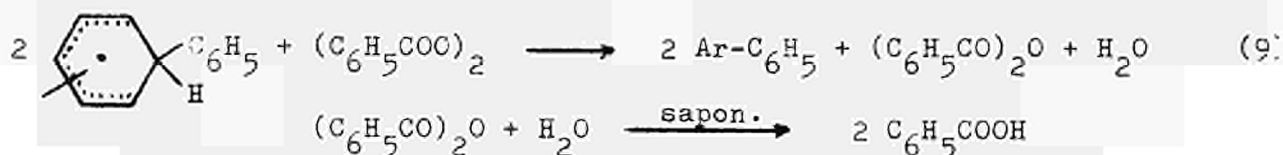
Yields of products in Mol/Mol peroxide

Solvent	CO <sub>2</sub>	1.Acid	Sum	2.Acid	Solvent-phenol	Phenylation product
benzene <sup>20)</sup>	-	0.319	-	-	0.020	0.37
benzene <sup>9)</sup>	1.34	0.42	1.76	0.25	0.09	0.29
chlorobenzene <sup>16)</sup>	-	0.42	-	-	0.049 <sup>*)</sup>	0.493
chlorobenzene <sup>10)</sup>	1.18	0.56	1.74	0.13	0.05	0.46
bromobenzene <sup>16)</sup>	-	0.962	-	-	0.021 <sup>*)</sup>	0.833
nitrobenzene <sup>18)</sup>	-	0.852	-	-	0.08	0.797
nitrobenzene <sup>10)</sup>	0.99	0.73	1.72	0.19	0.08	0.66
biphenyl <sup>5)</sup>	-	0.79	-	0.14	0.056 <sup>*)</sup>	-
biphenyl <sup>6)</sup>	0.92	0.79	1.71	0.24	0.05	0.64
biphenyl	1.00	0.74	1.74	-	-	0.69
o-terphenyl	1.00	0.74	1.74	0.14	0.067	0.76
m-terphenyl	0.96	0.78	1.74	-	-	0.816
methoxybenzene <sup>10)</sup>	0.51	1.22	1.73	-	-	0.36
naphthalene <sup>10)</sup>	0.42	0.95	1.37	0.42	0.24	0.40

<sup>\*)</sup> corrected for phenylbenzoate

groups, and in fact in many cases the "ester" acid is not only considerably less (around 6 or 7% only), but also is its amount in sharp contrast to the recovered rather small amounts of solvent phenols. It seems reasonable, therefore, to take only the phenol amount<sup>\*)</sup> or directly the respective ester as measure for the benzcarboxylation of the solvent. The differences observed experimentally are hardly significant, due to the low yields and the correspondingly high error involved. But if we consider the probably similar overall decomposition mechanism, the slightly increasing benzcarboxylation in the sequence bromobenzene < biphenyl < o-terphenyl is in line with the corresponding reactivities against phenyl radical. Despite the different mechanism the value for chlorobenzene seems rather high.

For p-dichlorobenzene, already Pausacker<sup>6)</sup> has noticed the above mentioned difference between recovered solvent phenol and the benzoic acid from saponification, and suggested that the  $\sigma$ -complex might be oxidized directly by benzoyl peroxide to give phenylation product and benzoic acid anhydride as additional precursor for benzoic acid.

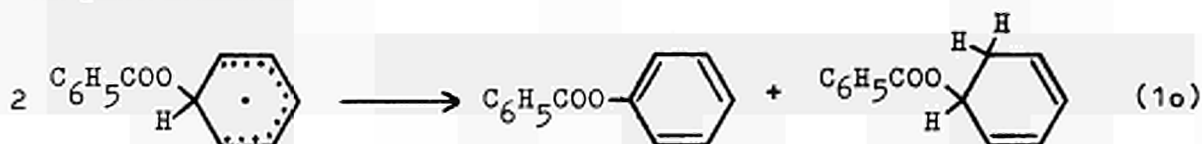


Little about benzoic acid anhydride has been mentioned in the literature, and it was also never especially searched for it. Russian authors<sup>24)</sup> reported no trace of the anhydride in the decomposition of benzoyl peroxide in benzene. Though Eliel and coworkers<sup>13),25)</sup> found evidence for the dehydrogenation of phenylcyclohexa-1,4-diene by benzoyl peroxide, they mentioned that "the process requires heat and the dehydrogenating species are thus presumably the carboxy radicals ArCOO<sup>•</sup> rather than the diaroyl

\*) Where in the literature a distinction was made between phenol or phenyl-benzoate and solvent phenol or solvent ester, the values have been corrected.

peroxides as such". We have found in our experiments always traces of water, which were flushed out of the reaction mixtures with the nitrogen stream, but we cannot exclude that they are still due to the very low water content of the used solvent. It might be, nevertheless, an indication for an oxidation process, which results in the formation of water.

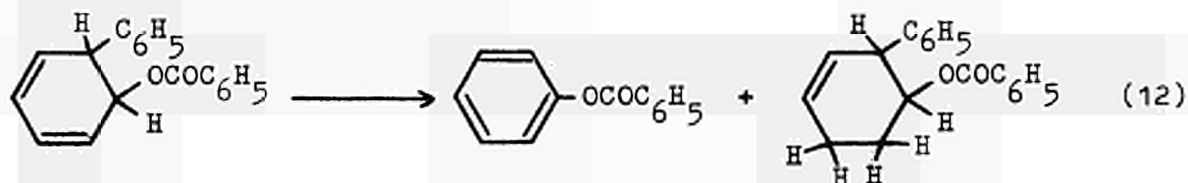
Another source of carboxyl groups from saponification independent of phenolic counterpart, are possibly aliphatic esters, as they might be produced in disproportionation of benzoyloxy- $\sigma$ -complex-radicals



or in the following quite probable combination reaction



It is in fact surprising, that esters of the last type have never been found so far. They might be thermo-labile and split off benzoic acid quite easily. The net effect is then the dehydrogenation of the phenyl- $\sigma$ -complex by the benzoyloxy-radical, giving biphenyl and benzoic acid. They could on the other hand also disproportionate to give aromatic ester and a more stable tetra-hydro-aromatic ester.



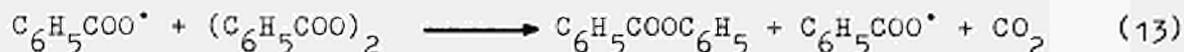
Saponification of these esters would then give aliphatic alcohols, undetected and hidden in the residue by the normal workup procedure. But in contrast to this Pausacker<sup>6)</sup> found the residue of the decomposition in dichlorobenzene oxygen free.

4.4.2. TOTAL PHENYL RADICAL PRODUCTION

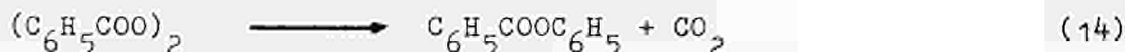
In the treatment of our experimental values we have suggested that the amount of carbon dioxide is a true measure of the phenyl radical production according to equation (3). All products which arise then from reactions involving phenyl radical could be related more truly to that basis rather than to benzoyl peroxide, especially, as our main interest was the actual phenylation process. The only reaction which would produce carbon dioxide and not concomitantly phenyl radical is a direct decomposition of the benzoyl peroxide to give phenylbenzoate. Davies, Hey and Williams<sup>5)</sup> observed the formation of small amounts of phenylbenzoate in chlorobenzene and in biphenyl, together with the expected chlorophenyl resp. biphenyl-benzoates.

Suggestions for possible mechanisms were already made earlier<sup>21),2),9)</sup>. In a recent publication, Gill and Williams<sup>16)</sup>, investigating kinetics and products of decomposition in chlorobenzene and bromobenzene, reported also a very low yield of phenylbenzoate. They mentioned three possible mechanisms:

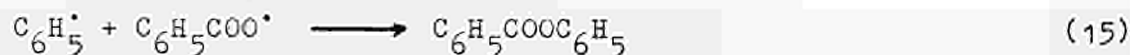
1) an induced reaction



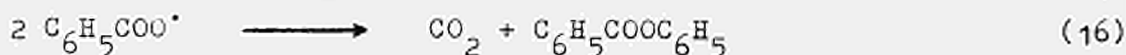
2) intramolecular decarboxylation



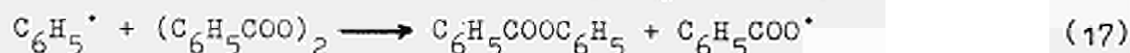
3) "cage" recombination



Additional possibilities<sup>21),5)</sup> are the radical combination



and an induced reaction with the phenyl radical



The cage recombination (15) would not directly influence the carbon dioxide-phenyl radical equivalence, as no extra carbon dioxide is liberated, but would exclude a part of the phenyl radicals from free selectivity. In any case the amount of this side reaction is so small, that it may be totally neglected in our determination of the phenyl radical yield. Gill and Williams<sup>16)</sup> found for both halo-benzenes around 0.01 mole ester per mole of peroxide, Davies, Hey and Williams<sup>5)</sup> the same for chlorobenzene and only 0.002 mole per mole peroxide in biphenyl. As the latter pointed out, the drop in phenylbenzoate formation from chlorobenzene to biphenyl could be explained by the higher reactivity of biphenyl, if equation (13) is followed. As we found that the terphenyls are even more reactive than biphenyl, the phenylbenzoate formation is probably further suppressed. Our somewhat higher decomposition temperature (100°C instead of 80°C) should not change this situation drastically. We did not determine esters and, therefore, cannot judge the proposed mechanisms<sup>\*)</sup>. From a determination of the concentration dependence of the phenylbenzoate yield a distinction between intramolecular decarboxylation (14) resp. cage recombination (15) and induced reactions (13), (17) or radical combination (16) is certainly possible. Recently, Gill and Williams<sup>18)</sup> found no increase in phenylbenzoate formation, when they added a small amount of nitrobenzene to benzoyl peroxide in benzene, though biphenyl was augmented appreciably. They concluded that therefore at least part of that ester

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\*) A differentiation between intramolecular decarboxylation (14) and cage recombination (15) seems to us not very plausible: Phenyl radical is very reactive towards solvent molecules. If it is not able to attack them in the solvent cage, its relation (or quasi-bonding) to the benzoyloxy-radical must be from the beginning so strong, that one might call the reaction an intramolecular decarboxylation as well.

must be formed directly from the peroxide and not through reactions in analogy to (4), (2) or (7)\*). This conclusion would mean that not only the "inevitable" part of phenylbenzoate - the part which is formed also in other solvents - is a product without solvent interaction, but maybe even all of it, as the phenylbenzoate yield in benzene<sup>20)</sup> is hardly double that in chlorobenzene and bromobenzene<sup>16)</sup>.

#### 4.4.3. FATE OF PHENYL RADICALS

Most of the produced phenyl radicals are found after the reaction in the form of phenylated solvent. The rise in recovered phenylation product from biphenyl to m-terphenyl in our experiments is in line with the increased reactivity and points to a decreasing incursion of side reactions. But just, what side reactions occur, is rather unclear. In the literature one finds practically never higher yields of phenylation products than 85% (rel. to carbon dioxide), and this figure includes already the correction for the eventual dimerization products of reaction (5), which are found in the high-boiling residue. In the recent works of Gill and Williams<sup>20), 16), 18)</sup> the carbon dioxide yield was not measured, nor was the "ester" acid determined and, therefore, the totally produced phenyl radical amount is unknown. Furthermore, the high-boiling residue was without analysis taken as the corresponding tetrahydro-quaterphenyls and included in the product sum-up, a method which is applicable to the well-investigated decompositions in benzene and chlorobenzene<sup>22)</sup> but not for the ones in bromobenzene and especially nitrobenzene without closer examination.

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\*) Another explanation is that in the presence of nitrobenzene much less benzoyloxycyclohexadienyl radicals are formed and any increase would therefore be possibly hidden.



We did not determine the amount of high-boiling material or of labile dihydro compounds in our reaction mixtures, but according to the foregoing discussion we may conclude that the lower percentages of recovered phenyl radical for biphenyl - (67%) and o-terphenyl- (75%), as compared to m-terphenyl-phenylation (83%), are possibly the consequence of a higher yield of these compounds. Tetra-hydro-hexaphenyls and tetra-hydro-octaphenyls could be expected from biphenyl and terphenyl phenylation, resp. As tetra-hydro-quaterphenyls are decomposing above about 130°C into biphenyl and dihydrobiphenyls<sup>26),20)</sup> one might recover in our cases corresponding decomposition products, namely terphenyls and dihydro-terphenyls, and quaterphenyls and dihydro-quaterphenyls, respectively. It has been already discussed in the literature<sup>20),25)</sup>, that the dihydro-cyclohexadiene compounds might be removed rapidly by such processes as radical polymerization, addition of a radical to a double bond or hydrogen abstraction. Therefore a part of the phenyl radicals might be caught in high-molecular and polymeric material in the high-boiling residue. As we analysed exclusively by gas chromatography at a column inlet temperature of 290°C, it is possible that any dihydro- or tetra-hydro-polyphenyls, present in the reaction solution, are destroyed immediately by polymerization, when they reach the hot column material and only the stable polyphenyls themselves survive\*).

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\*) The behavior of dihydro- or tetra-hydro-polyphenyls in gas chromatography is till now not known. (B. Versino, CCR Ispra, private communication).

It is very interesting to compare for this question the yield of high-boiling residue found by Karelsky and Pausacker<sup>6)</sup> in the decomposition in biphenyl at a somewhat higher concentration and lower temperature<sup>\*)</sup>. If we take this residue entirely as tetra-hydro-hexaphenyls, the product of dimerization of the  $\sigma$ -complex, we raise the percentage of recovered phenyl radicals to around 85%, a value close to that for m-terphenyl. As in o- and m-terphenyl less benzoic acid is produced than phenylated solvent, another dehydrogenation mechanism besides reaction (7) must be operative as well.

Benzoyl peroxide (as dehydrogenating agent) can be excluded, because the sum of carbon dioxide and benzoic acid is constant for all three polyphenyls. We must conclude, therefore, that the disproportionation reaction of the  $\sigma$ -complex (6) is preferred over the dimerization (5), or that the tetra-hydro-octaphenyls are more thermolabile than the tetra-hydro-hexaphenyls and decompose by disproportionation. This would be understandable by the bigger molecule size and by reasons outlined above for the dehydrogenation by benzoyloxy-radical. It has been already mentioned, that the phenyl radical could in principle also abstract hydrogen from the  $\sigma$ -complex, but that the stationary concentration of both partners might be too low. In any event, we can say that for this extra dehydrogenation, given by the difference between benzoic acid yield and yield of phenylated solvent, an equal amount of phenyl radical or phenyl radical derived compound has been used. This would bring the phenyl radical yield, accounted for in products, to 81% for o-terphenyl and 92% for m-terphenyl. A high-boiling residue, which contains dimerization products could still be present especially in o-terphenyl solution.

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\*) J.I.G.Cadogan, J.H.Hey and G.H.Williams<sup>4)</sup> report no high-boiling residue for biphenyl phenylation.

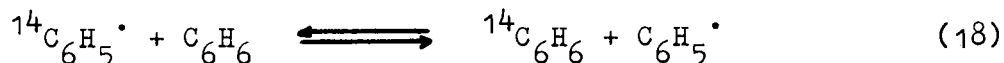
This leads immediately to the question, if not with such uncomplete dehydrogenation the final isomer composition of the quaterphenyls is different from what it should be by the primary selection of the positions by phenyl radical. As has been shown by others<sup>14)</sup> and will be discussed in this work later, the isomer relation seems unaffected by the presence or absence of disproportionation and dimerization reactions.

A source of phenyl radical loss which has hardly been considered in literature is the formation of low-boiling compounds, especially of benzene. We found qualitatively benzene from biphenyl, o- and m-terphenyl and a very small amount of biphenyl<sup>\*)</sup> from o- and m-terphenyl. The only indications for the occurrence of such reactions come from the works of E.L.Eliel and coworkers<sup>13)</sup> and of the Russian group of G.A.Razuvaev<sup>27)</sup>. The first noted a certain inconsistency of their results from the benzoyl peroxide decomposition in deuterated benzene, which was only to overcome on the assumption that a small part of the biphenyl was derived entirely from phenyl groups of benzoyl peroxide, and that some undeuterated benzene was formed as well. They obtained indeed benzene and biphenyl in small amounts, when they decomposed the peroxide in chlorobenzene. The occurrence of a little biphenyl in this case was also reported by Davies, Hey and Williams<sup>5)</sup> and recently again by Gill and Williams<sup>16)</sup>. G.A.Razuvaev's group used very high concentrations (0.9-1.0 molar) of <sup>14</sup>C-labelled benzoyl peroxide in inactive benzene or of inactive benzoyl peroxide in <sup>14</sup>C-labelled benzene. They found in accordance with Eliel's deuterium experiments that more phenyl groups in the resulting biphenyl were derived from benzoyl peroxide than from benzene and furthermore that an appreciable part of the activity had spread into the originally inactive benzene. E.L.Eliel did not discuss the benzene production

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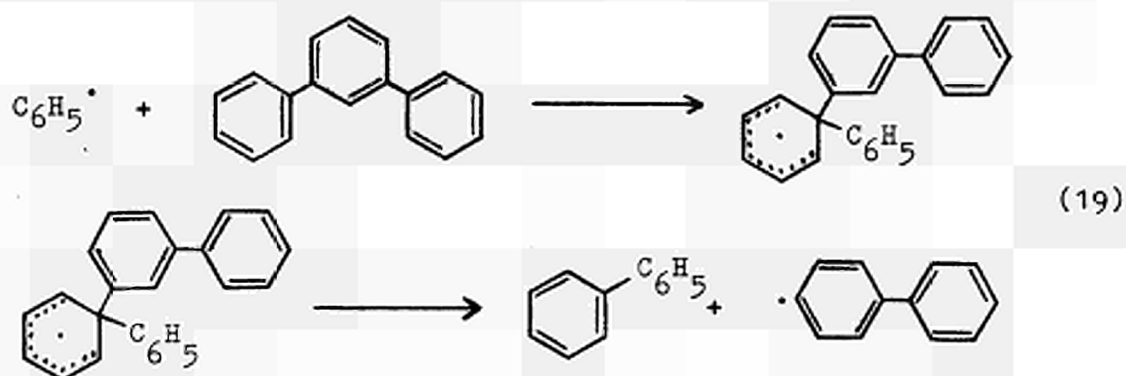
\*) The identification of biphenyl in the gas chromatographic analysis was by retention time only and is therefore a little dubious.

from chlorobenzene. The Russian authors explained their results by the radical exchange reaction:



This would ascribe our benzene formation to a hydrogen abstraction from the aromatic polyphenyl solvent by phenyl radical. The activation energy for such a process is certainly much higher than for the normal addition reaction and no energy gain is involved, too. More probable should be even hydrogen abstraction from benzoic acid, which is present in rather high concentration towards the end of the reaction. The O-H bond is on the other hand probably still too strong to allow an attack of the phenyl radical. Much more labile H-atoms in benzylic and allylic positions are present, not only in the cyclohexadiene- $\sigma$ -complexes, whose stationary concentration is maybe too low in the polyphenyls for an abstraction, but also in the form of dihydro- or tetra-hydro-cyclohexadiene compounds. In benzene as solvent these compounds are present even in relatively high amounts. The rather low concentration of these compounds in the polyphenyls could well be made up by the low activation energies for their H-abstraction. In the benzoyl peroxide decomposition in alkylbenzenes<sup>28)</sup> the percentage of H-abstraction relative to addition to the nucleus rises in the order toluene (13%), ethylbenzene (55%), isopropyl-benzene (60.5%) and is in accordance with the lower bond strength of the benzylic CH-bonds. The combination of benzylic and allylic positions will promote the abstraction even more. That on the other hand the phenyl radical shows also the necessary selectivity is obvious not only from the above results with alkylbenzenes, but quite generally from the existence of a reactivity scale with aromatic compounds and with individual positions in a given aromatic.

That the corresponding kinetic lifetime of the phenyl radical might be nevertheless too short and consequently the stationary concentration too low to allow a dimerization to biphenyl was mentioned by Gill and Williams<sup>16)</sup>. They, like already earlier E.L.Eliel<sup>13)</sup> explained its formation in chlorobenzene rather by phenyl radical attack in position 1 of chlorobenzene and subsequent chlorine transfer and dehydrochlorination. No biphenyl was detected from bromobenzene in Gill and Williams' work. The corresponding process for the terphenyls



seems not very likely due to steric reasons and the low free valence at the attacked position.

The very small yields of biphenyl, obtained in our experiments, could be produced without interaction of the solvent and both phenyl groups must then be derived from benzoyl peroxide. Razuvaev<sup>27)</sup> did not discuss the rather high percentage of phenyl groups from benzoyl peroxide in his biphenyl. His result was probably due to the very high concentration used, and could arise in this case indeed by phenyl radical dimerization. Eliel's concentration in chlorobenzene (0.4 mole/liter) and our concentration (0.2 mole/liter) might still allow a tiny production by this reaction. A further possibility is a certain intra-molecular process, as in the decomposition of benzoyl peroxide by UV-light, where both nuclei of biphenyl are taken from the peroxide.

The best explanation for the biphenyl production would certainly be a normal phenylation process with the benzene, produced during the decomposition. As we do not know the quantity of benzene, we cannot judge, if the necessary concentration is available, to balance the approximately 4 resp. 5 times lower reactivity of

The phenylation of products, especially of the phenylated aromatic needs further discussion. In benzene, the isomeric terphenyls<sup>2),22)</sup> and phenyl benzoic acid are the results of phenyl radical attack on biphenyl and benzoic acid, respectively. We found in our biphenyl-reaction solutions traces of all isomeric quaterphenyls and in all our acid extracts small amounts of phenylbenzoic acid. The effectiveness of these phenylations is controlled by the benzoyl peroxide concentration or more accurately, because the solvent is a reactant, by the molar ratio and the relative reactivity as compared to the solvent. The value for benzoic acid is unknown, but possibly around the one for the methylester (2.4 compared to benzene<sup>2)</sup>). The first phenylation product is generally always higher reactive than the starting material, though in different relations, as can be seen from our reactivity scale of the polyphenyls and the relative value of 2.94 for biphenyl, determined by Hey<sup>7)</sup> (benzene = 1). From these reactivities and the yields of the first phenylation product one can make a rough calculation of the importance of the "secondary" phenylation<sup>\*)</sup>. Though biphenyl is 2.94 times more reactive than the starting material benzene, hardly more than 1% of all phenyl radicals react with it, due to a low overall biphenyl yield, whereas with the only around 1.7 times more reactive terphenyls, compared to biphenyl, a secondary phenylation with about 2% of the phenyl radicals should be expected. This calculation is based on equal benzoyl peroxide concentrations and the reactivity value for m-terphenyl taken as representing the isomeric terphenyl mixture. If we take for the benzene

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\*) Example of calculation: We take half the amount of the endproduct as "average concentration", which approximates quite well the slow build-up of the product during the decomposition. The molar ratio between that amount and the solvent multiplied by the relative reactivity gives the factor for the "secondary" phenylation or multiplied with 100 the percentage of phenyl radicals reacting with the product.

solution the same molar ratio of benzoyl peroxide to solvent as for biphenyl (0.03), which affords a 35% higher concentration, still not more than 1.8% of all phenyl radicals would give terphenyls.

We do not know the reactivities of quaterphenyls and cannot calculate therefore the contribution of the second phenylations. But if the reactivities are not appreciably higher, which is unlikely (see later), than those of the terphenyls, the secondary phenylation would not consume more than 3% of the phenyl radicals. A similar calculation for the phenylation of the produced benzoic acid in benzene, biphenyl and o- and m-terphenyl as solvents reveals that rather equal amounts of between 0.8-0.9%<sup>\*)</sup> of the phenyl radicals phenylate the acid.

A similar result can be estimated for an attack on the benzoyl peroxide itself, a process which has been proposed earlier<sup>5)</sup>. The calculations show that the phenylation of starting material and products for the discussed cases is relatively unimportant in comparison to the other side reactions, mentioned above, whereas at very high concentrations and especially with substituted peroxides the product composition might be considerably changed.

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<sup>\*)</sup> 0.9% in benzene, 0.85% in biphenyl, 0.92% in o-terphenyl, 0.77% in m-terphenyl.

#### 4.5. RELATIVE REACTIVITIES AND PARTIAL RATE FACTORS

##### 4.5.1. INDEPENDENCE OF REACTIONS IN MIXED SOLVENTS

An interesting feature of the experiments in mixed polyphenyl solvent is that the phenylation of each of the solvents is not influenced by the other. This can be seen qualitatively from the combined yields of phenylated solvent 1 and 2, which lie around the middle between the yields for the pure compounds. The best proof is that the sum of phenylated solvent and the calculated yield of phenyl radical-derived byproducts adds up in the biphenyl/o-terphenyl and biphenyl/m-terphenyl experiments to almost the originally produced phenyl radical amount (table IV). This shows that none of either side-reaction is influenced by the presence of a second, even more reactive compound, which could have been attacked in preference to a side-path. The result would have been a higher phenylated solvent 1 to byproduct ratio as compared to that of the pure solvent 1. On the other hand the actual drop in byproduct of solvent 2 would not become obvious, because its amount is calculated. Experimentally more phenylated solvent 1 would have been found and consequently the calculation of its byproduct would have been too high. This combined real and "false" increase of products from solvent 1 would have lifted the total sum of phenylation products immediately over the theoretical maximum, given by the carbon dioxide, i.e. phenyl radical yield, and therefore become obvious.

The slightly lower values of the sum of all phenyl radical-derived products from biphenyl/o-terphenyl and biphenyl/m-terphenyl experiments as compared to the phenyl radical yield are hardly significant at all, because the experimental error of the carbon dioxide determination is already about  $\pm 3\%$ . Lower values for the sum up must be expected, if more byproduct is formed on the expense of any of the phenylated derivatives.



It has been stated in the literature<sup>2)</sup> that the presence of a "fast" solvent, like nitrobenzene, would suppress the side-reactions, e.g. dimerization etc., of the first, less reactive solvent. This seems to be possibly valid for nitrobenzene or aromatic nitro-compounds only, which are probably an exception by their special reaction mechanism<sup>18)</sup>. Biphenyl, which has the same reactivity as nitrobenzene, would in a mixture with benzene allow the best check of the above statement. A good indication for a product-change, whenever benzene is involved, is the amount of produced "first" benzoic acid. Gill and Williams<sup>18)</sup> found that even on the addition of only small amounts of nitrobenzene (1:100) to a benzoyl peroxide solution in benzene, this benzoic acid yield is already as high as for pure nitrobenzene and signals already the increased biphenyl yield. We have made preliminary investigations on the yields of carbon dioxide and benzoic acid (table I) for the 1:1 molar mixtures of benzene with biphenyl, o- and m-terphenyl. The benzoic acid values were in between those for the pure compounds and always appreciably away from those of the polyphenyls alone. We assume therefore that even with such differently reactive solvents as benzene and m-terphenyl no interference or mixture of the two phenylation processes takes place. At least for our investigations we can conclude from this fact once more that side-reactions leading to byproducts occur mainly after the primary selection and addition of the phenyl radical to the solvent, i.e. after the formation of the  $\sigma$ -complexes. For them mutual interaction is of course possible. For instance "cross"-dimerization and "crossed" disproportionation might be certainly allowed. The formation of benzene is too insufficiently known to make any prediction in this connection.

#### 4.5.2. DETERMINATION OF RELATIVE RATE CONSTANTS

The above conclusion that the addition of the phenyl radical to one of the two aromatic solvents is the first step for the main phenylation and the side-reactions, is very important for the determination of a correct and generally valid value for the relative rate constant. It shows that one must use the sums of main and side-reactions of each solvent to obtain the correct relation of phenyl radical attack. As has been stated already, Hey's method of taking only the relation of phenylated solvents would be in error, whenever any side-products are formed. His goal is therefore to investigate mixtures where no side-reactions occur, for instance by suppressing them with nitrobenzene. For our method it is of fundamental importance that no mutual influence of the two phenylations exists and we could probably not treat mixtures where one component is a nitro-aromatic compound. Therefore both methods have their special field of application. It must be mentioned, though, that Gill and Williams' results<sup>18)</sup> of the benzoyl peroxide decomposition in nitrobenzene show clearly also side-reactions for this solvent by its definite amount of high-boiling residue. These side-reactions - different in nature from those in benzene - will not be suppressed in the mixtures like those of its partners, only maybe changed in its amount to some extent, and could lead to false calculations of the reactivities.

We cannot relate our reactivities to benzene and the corresponding reactivity scale of benzene derivatives, because of the temperature-difference of our and Hey's competition experiments (100°C and 80°C respectively), and because the existence of a temperature-dependence of the reactivities cannot be excluded. For the slight difference in temperature, though, one would not expect a drastic change and we can discuss at least qualitatively the change of reactivity from benzene to the terphenyls.

In the homolytic substitution of aromatic compounds it has become evident<sup>2)</sup> that the selectivity of the phenyl radical is connected with the resonance stabilization of the produced  $\sigma$ -complex radical or rather with the free valence values of the aromatic reactant. The big jump in reactivity from benzene to biphenyl (around 1:3) is not repeated between biphenyl and the two investigated terphenyls. This was expected, because the presence of a third phenyl ring does not again introduce newly the opportunity for resonance, as with biphenyl, where six out of the ten possible substitution positions allow now resonance for the  $\sigma$ -radical (leading to o- and p-substitution). In the terphenyls are offered additional possibilities for the resonance with the third ring when substituting certain positions in the terphenyl-molecule. Though o-terphenyl has six positions available for this additional effect (four leading to o,o-quaterphenyl, two to o,p-quaterphenyl) and m-terphenyl only three (two leading to 1,2,4-triphenylbenzene, one to 1,2,3-triphenylbenzene) the reactivities show the reverse order and are 1.40 and 1.66, respectively. Two reasons might be responsible:

- 1) steric hindrance for the attack in the positions leading to o,o-quaterphenyl<sup>\*)</sup>.
- 2) decreased possibility of resonance because of uncomplete planarity between the cyclohexadienyl- and the biphenyl-system.

For the reactivity of the p-isomer we can make a first rough estimation. We have like in the o-terphenyl again six positions, where a radical attack leads to an electron distribution over both two other phenyl rings but no steric hindrance or obvious nonplanarity. The reactivity should, therefore, be certainly higher than for m-terphenyl and a value of over 2 might be expected.

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\*) The atomic model shows that two of the four positions in o-terphenyl, which lead on substitution to o,o-quaterphenyl should be totally hindered.

Still more difficult is a prediction of the reactivities of the various quaterphenyls and triphenylbenzenes, because the influence of an additional phenyl group is unknown, especially when steric hindrance comes into play. A detailed discussion follows below in connection with the partial rate factors.

#### 4.5.3. ISOMER DISTRIBUTION AND PARTIAL RATE FACTORS

Cadogan, Hey and Williams<sup>4)</sup> have reported isomer values of 48.5, 23 and 28.5% for o-, m- and p-terphenyl, respectively, in the phenylation of biphenyl. Our values are only slightly different: the p-terphenyl amount (32.2) is increased at the expense of the o-isomer yield (44.8), m-terphenyl is the same. This change can at least partly be attributed to the 20° higher decomposition temperature (100° versus 80°), because decreasing o-substitution with increasing temperature has been reported and explained by Williams<sup>2)</sup>. The partial rate factors, related to benzene, for the biphenyl phenylation as calculated by the above authors and corrected later by Hey, Orman and Williams<sup>7)</sup> show that the m-position is not activated at all and has the value 1.0. The total reactivity gain over benzene (2.94) comes therefore from the activation of the o- and p-position (2.1 and 2.5, respectively), with the p-position only a little favored. Though according to free valence calculations the o-position should be by far preferred, steric hindrance is most probably the reason for the inverse relation. If we calculate the partial rate factors for our values despite the temperature difference of the experiments we arrive at 1.95, 1.0 and 2.8 for o-, m- and p-attack, respectively.

As has been mentioned in the experimental part, a complete isomer separation and analysis for the terphenyl phenylation was only possible for the pure m-terphenyl and the m-terphenyl/biphenyl mixture. From the phenylation of o-terphenyl and its admixture with biphenyl we have three isomer ratios for the quaterphenyls instead of the expected five. That all the isomer ratios are practically the same for the pure terphenyls and for their mixtures with biphenyl, proves again the independence of each phenylation reaction from the other under our conditions. On the other hand this constancy is not surprising, because it has been shown by numerous examples in the literature<sup>2)</sup> that the isomer relation is the least sensitive result of a phenylation. It is not only constant, if one changes the reaction conditions by using different concentrations<sup>16)</sup> or adding oxygen<sup>17)</sup>, which effects the yields of phenylation products appreciably, but it stays even constant, if one uses different sources for the phenyl radical<sup>2)</sup>, and homogeneous or heterogeneous solutions<sup>2)</sup>. This constancy was the main argument for Hey and his coworkers in demonstrating that their determination of reactivities was correct, because obviously any byproduct formation by further reaction of the different  $\sigma$ -complex radicals is not selective. This seems to be true also for disproportionation reactions<sup>14)</sup> and therefore no false isomer relation would arise in the case of o- and m-terphenyl phenylation, where part of the dehydrogenation is by such reactions. Our criticism of Hey's reactivity determination is not concerned with this question of the isomer relations but with that of the total relative rate constant and consequently the partial rate factors, which are calculated from them. Our argument is that the amount of byproduct formation is specific for a certain aromatic solvent and is normally unchanged in a competition experiment. If the byproduct amount is not equal for the

two competing solvents or nil, the determination from the yields of phenylated solvents alone is definitely wrong. In our cases the calculation, following the procedure of Hey, would give the following values: 1.55 instead of 1.40 for o-terphenyl, 2.06 instead of 1.66 for m-terphenyl, both relative to biphenyl, and 1.32 instead of 1.18 experimentally and calculated for the m-terphenyl/o-terphenyl reactivity.

The isomer distribution from the phenylation of m-terphenyl allows interesting conclusions about the importance of mesomeric, inductive and steric effects in homolytic substitution. For better comparison one must first determine the participation of each nuclear position in the phenylation, taking into account that different numbers of positions are available for the formation of the six isomers (table VI, column 1). By dividing the isomer percentage by the number of identical positions one arrives at the number of phenyl radicals out of 100, which react with one specific position (column 2). For a more general comparison Augood, Hey and Williams<sup>17)</sup> have introduced the "partial rate factor", which relates the specific activity of a certain nuclear position of any aromatic compound to one of the six equal positions in benzene (= 1). To be independent from the previously mentioned biphenyl reactivity of 2.94 of Hey's group and not to mix experimental data, which were obtained for different temperatures, we could have chosen as a reference for instance the m-positions in the biphenyl molecule and given it the value  $k_m = 1.00$  ( $K_{\text{biphenyl}}$  would then be 17.4). As accidentally the m-position in biphenyl compared to one position in benzene, i.e. the partial rate factor for m-substitution in biphenyl, as determined by Hey<sup>6)</sup>, has almost exactly the value 1.0, the same partial rate factors for the m-terphenyl-phenylation result with each standard (column 3). The next columns in the table give the resonance possibilities in the  $\sigma$ -complex-radical, steric hindrance and whether substitution is in the outer or central phenyl group.

TABLE VI Partial rate factors and structural characteristics in the phenylation of terphenyls

Produced Isomer	Positions available	% Reaction per Position (experim.)	Partial Rate Factors	Phenyl Groups for Resonance in $\sigma$ -complex	Steric Hindrance	Substitution in outer/central Ring
from m-terphenyl						
1,2,4-TPB	2	15.2	4.4	2	+	central
1,2,3-TPB	1	12.3	3.5	2	++	central
m,p- $\phi_4$	2	9.2	2.7	1	-	outer
o,m- $\phi_4$	4	6.2	1.8	1	+	outer
1,3,5- $\phi_4$	1	4.0	1.2	0	-	central
m,m- $\phi_4$	4	2.8	0.8	0	-	outer
from o-terphenyl						
1,2,4-TPB	2		(2.9)	1	-	central
+ o,p- $\phi_4$	2	11.8	2.9	2	-	outer
o,m- $\phi_4$	4	5.5	1.4	0	-	outer
1,2,3-TPB	2		(2.0)	1	+	central
+ o,o- $\phi_4$	4	5.2	1.3	2	++	outer
calculated for p-terphenyl ( $k_m = 1.0$ )						
p,p- $\phi_4$	2	-	(5.1)	2	-	outer
o,p- $\phi_4$	4	-	(4.2)	2	+	outer
1,2,4-TPB	4	-	(2.4)	1	+	central
m,p- $\phi_4$	4	-	1.0	0	-	outer

The following conclusions can be drawn from the sequence in the partial rate factors: The most important quality for the selection of a certain position is a pronounced resonance-stabilization for the resulting  $\sigma$ -complex-radical or, what is more interesting for the immediate attack, a high free valence in this position. Mesomeric distribution of the single electron into one more phenyl ring rises the partial rate factor from 1.8 to 4.4 in going from o,m-quaterphenyl to 1,2,4-triphenylbenzene formation. For this high increase of 2.6 - we must compare with the o-position in biphenyl - is partly also responsible the substitution in the central ring, when forming 1,2,4-triphenylbenzene. This is clear from a comparison of the values for m,m-quaterphenyl and 1,3,5-triphenylbenzene (difference 0.4). The central ring is slightly activated, possibly through inductive effect of the two phenyl groups. The four meta-positions are on the other hand a little less reactive than in biphenyl or than any position in benzene. Therefore the actual rise for the action of the second phenyl ring should be around 2.0 to 2.2. The pair m,m-quaterphenyl/m,p-quaterphenyl - both times substitution in the outer ring only - can be correlated with m-substitution/p-substitution in biphenyl. Almost the same difference of 1.8-1.9 between the partial rate factors is found for both sets of values. The steric hindrance is of less importance. This can be deducted from the values of o,m-quaterphenyl/m,p-quaterphenyl and 1,2,4-triphenylbenzene/1,2,3-triphenylbenzene. The former two resemble o- and p-substitution in biphenyl, which differs by 0.8. For both pairs the difference of 0.9 is the consequence of the steric hindrance, which proves that a position flanked by two phenyl groups is exactly doubly hindered.



Accordingly, the three guiding factors for preferential attack in a certain nuclear position and their numerical contributions are in decreasing order of importance;

- 1) number of phenyl groups for resonance stabilization (1.9 for the first and 2.2 for the second phenyl group),
- 2) steric hindrance by o-positioned substituents (0.8-0.9 for each phenyl group),
- 3) inductive activation of a nucleus by the presence of two m-attached phenyl groups (0.4).

The good correlation found for these influences justifies the assumption that their numerical values, given in brackets, have a more general validity. With these figures one can calculate quite accurately from one of the partial rate factors of the m-terphenyl derived isomers all the others. For instance, to find from the value for the 1,3,5-triphenylbenzene (1.2) the one for 1,2,4-triphenylbenzene we add for the resonance effect 1.9 for the first phenyl group and 2.2 for the second and deduct 0.9 for the steric hindrance, which gives 4.4.

For the o-terphenyl phenylation we cannot make such a distinct differentiation, because two isomer pairs could not be separated (see table). Furthermore, o-terphenyl is probably a special case, because, as has been already mentioned, a planar configuration of the  $\sigma$ -complex-radical for maximum resonance with two phenyl groups is not anymore possible. The only partial rate factor we can calculate specifically is the one for o,m-quaterphenyl formation. The 1.4 obtained, seem high compared to the m-position value in biphenyl (1.0) and the m,m-quaterphenyl in m-terphenyl (0.8) and could point to an increased inductive activation by the attached biphenyl group, as a consequence of the nonplanarity of allyl and aromatic system. The diminished effect of resonance in the phenylation of o-terphenyl is proved by the combined partial rate factor of only 1.3 for 1,2,3-triphenylbenzene and o,o-quaterphenyl formation, though one and two phenyl groups,

respectively, could have been used for resonance. What is maybe left of the mesomeric effect is not even enough to counteract the steric hindrance, which is involved on all six positions under discussion. Also without steric hindrance the partial rate factor is much lower than it should be by the extensive use of resonance stabilization. This can be seen on the 2.9 for 1,2,4-triphenylbenzene and o,p-quaterphenyl formation. We estimate that the rest of resonance stabilization contributes 0.9 for the first and 0.6 for the second ring to the partial rate factor and that the steric hindrance in the o,o-positions is slightly higher than in a position flanked by two phenyl groups. The inductive influence contributes 0.6 already for the first ring if we compare m-substitution in the outer rings of o- and m-terphenyl, respectively, and we estimate the same contribution for the second one. We can make then a rough calculation of the partial rate factors in the two isomer pairs by using the o,m-quaterphenyl value. The values are given in brackets in table VI.

We have an indication from the gas chromatographic analysis, that 1,2,4-triphenylbenzene and o,p-quaterphenyl are indeed present in approximately equal amounts in the reaction mixture. The value of 1.0 for the substitution in the o,o-positions is very low, because of the extreme steric hindrance in two of the four o,o-positions. In fact, if we do not consider this steric hindrance, but only the one for o-substitution of biphenyl (value 0.9) we get a value of 2.0 for the partial rate factor and this is exactly, what we expect, if the two positions would not react at all. The o-terphenyl behaves for the formation of the o,o-quaterphenyl isomer, as if only two nuclear positions would be available.

We can conclude now that for the phenylation of o-terphenyl steric factors become as important as resonance stabilization and that inductive influences are a little more important compared to m-terphenyl. The cause for this specialty is a pronounced non-planarity of o-terphenyl and especially of its  $\sigma$ -complex radical system.

By taking the numerical values found for the different influences on the partial rate factor for the m-terphenyl phenylation, we can now make a calculation of the partial rate factors for the p-terphenyl phenylation and a better prediction of the total reactivity for p-terphenyl. We must fix one partial rate factor and may take for that purpose the m-positions in the outer ring, as they have the lowest values and are least activated. This position is 0.8 for m-terphenyl and can be somewhat different for the p-isomer. We chose 1.0 for  $k_m$  which gives consequently somewhat higher values for the partial rate factors (see table). The relative reactivity is then calculated to be  $2.3^*$  (relative to biphenyl), which shows that p-terphenyl should be by far the most reactive of the three terphenyls. It is interesting to note, that p,p-quaterphenyl should be formed in the highest yield (25%) followed closely by o,p-quaterphenyl (21%).

A prediction of the reactivities for the various quaterphenyls and triphenylbenzenes is much more difficult. Neither do we know how much the additional resonance possibilities of a third ring will be used, nor to what extent extreme steric hindrance suppresses such a resonance then, due to nonplanarity of the radical intermediate. For a rough estimation we may attribute to the unknown influence of the third phenyl group a value of 2.0 when no steric hindrance is operative. With an o,o-phenyl-configuration this value could drop to

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\*) If choosing 0.8 for  $k_m$  the relative reactivity becomes only slightly smaller (2.2).

around 0.4 (compare o-terphenyl). Furthermore, we might allow for the inductive influence in sterically highly hindered polyphenyls 0.6 for each phenyl group (see again o-terphenyl). With the use of the partial rate factors of the three terphenyls we are able to calculate then the values for quaterphenyls and the triphenylbenzenes. The most reliable figures of such an estimation are probably those, where no extreme steric hindrance complicates the situation. No matter how wrong the numerical values could possibly be, the relations are most probably correct and the sequence of reactivity should be: p,p-quaterphenyl (4.0)  $\gg$  m,p-quaterphenyl (2.7) > o,p-quaterphenyl (2.6) > m,m-quaterphenyl (2.4), 1,2,4-triphenylbenzene (2.3), 1,3,5-triphenylbenzene (2.3), o,o-quaterphenyl (2.3) > o,m-quaterphenyl (2.0)  $\gg$  1,2,3-triphenylbenzene (1.7).

## 5. CONCLUSION

We have seen that the phenylation of terphenyls leads mainly to the next phenylhomologs, the different isomers of quaterphenyl and triphenylbenzene. Out of a terphenyl mixture the p-isomer is the one most readily attacked by a phenyl radical, but the differences in reactivities are small, and the effect of concentration is still dominating by far. In a solution with 25% p-, 35% m- and 40% o-terphenyl the differences in reactivities are exactly matched and phenyl radical attacks all three terphenyls equally. As a similar reactivity scale exists for methyl radical and cyclohexyl radical<sup>28)</sup>, we can more generally conclude that also other reactive radicals attack the terphenyls according to the sequence p-terphenyl, m-terphenyl and o-terphenyl (in decreasing order).

This result for the phenylation at 100°C shows a pronounced difference to the sequence of terphenyl stability found in the pyrolysis or radiopyrolysis. There, o-terphenyl is least stable followed by p- and m-terphenyl. This does not exclude, that even during pyrolysis a similar initial mechanism, i.e. phenylation of the initially present solvent molecules after homolytic CC-bond ruptures between the aromatic rings might take place. The differences observed could rather be attributed to the much higher temperature, being involved in pyrolysis. It might be responsible for different reaction paths of the initially formed phenyl intermediates and for consecutive and chain reactions of the reaction products formed during a phenylation reaction. Also the simultaneous action of hydrogen radicals, being produced during high temperatures degradation of polyphenyls might at least in part account for the differences observed.

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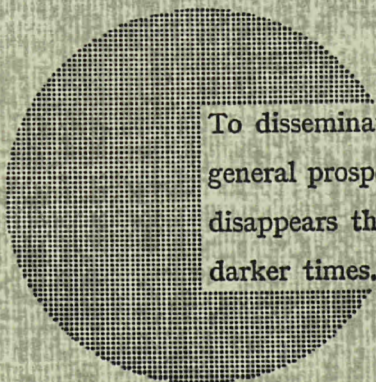
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